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PROCEEDINGS OF

THE ROYAL SOCIETY.

Section A.—Mathematical and Physical Sciences.

Optical Dispersion: A Comparison of the Maxima of Absorption and Selective Reflection for Certain Substances.

By T. H. Havelock, M.A., D.Sc., Armstrong College, Newcastle-on-Tyne.

(Communicated by Prof. Sir J. Larmor, Sec. R.S. Received August 8,—Read November 9, 1911.)

Introduction and Summary.

In the comparison of optical dispersion formulæ with experimental results, it is important to consider the meaning of the various constants, and in particular of the natural wave-lengths which occur in them.

With the formula in the simple form $n^2-1=\Sigma C_1/(\lambda^2-\lambda_1^2)$, the quantities λ_1 are the wave-lengths of the natural vibrations and have been identified in practice indiscriminately with the wave-length of maximum absorption or that of selective reflection obtained by the method of residual rays. This interpretation is allowable if the absorption is very small. For a more general type of formula such as $(n^2-1)/(n^2+a)=\Sigma C_1/(\lambda^2-\lambda_1^2)$, the corresponding wave-length, on a similar argument, for small absorption is a certain wave-length λ_1', which is larger than λ_1; in a previous paper* numerical examples were given of the difference between the wave-lengths λ_1 and λ_1'. The present paper includes absorption more generally in the formulæ, so as to determine the position of the various maxima more accurately.

Using dispersion formulæ of a general type, an expression is found for the position of the maximum of κ, the coefficient of extinction; further, a quartic equation is obtained, three of whose roots give the maximum of $n\kappa$, and the minimum and maximum of the refractive index n. The next step is to consider numerical examples of these formulæ. We choose first a substance for which the dispersion and absorption have been measured, namely, iodeosin; for this we calculate the positions of the various maxima and compare with experimental results. The remaining examples are carbon disulphide, rock salt, and sodium vapour. For these substances dispersion formulæ are known in a form not involving absorption; the formulæ have been completed by introducing coefficients of suitable value, and the maxima of absorption and of selective reflection have then been determined. The results illustrate the differences that may exist between these wave-lengths and the wave-lengths λ_1 of the simple dispersion formula; in the infra-red especially, where reflective power is large, the maximum of selective reflection is proved in general to be displaced considerably from the natural wave-length λ_1 or from the position of maximum absorption.

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* 'Roy. Soc. Proc.,' A, 1911, vol. 84, p. 512.

Derivation of Formulæ for Maxima.

Although there are various physical theories of the mechanism of absorption, such as those of Lorentz and Planck, the final formulæ are of the same form as those obtained by introducing a simple frictional term into the equation of motion of the vibrating particle.

In terms of frequency p, where the time factor has been made e^{ipt}, the complete dispersion formula is

$$\frac{1}{\sigma+1/(\mathfrak{n}^2-1)} = \Sigma_s \frac{C_s}{p_s^2-p^2+ib_sp}, \tag{1}$$

where $\mathfrak{n} = n(1-i\kappa)$. The quantity σ is a constant: two special types are obtained by making it zero, or $\frac{1}{3}$; p_s is the frequency of the natural undamped vibrations. If we consider the vibrating particle to be of mass m_s and to carry a charge e_s, we have C_s equal to $4\pi N_s e_s^2/m_s$, where N_s is the number of such particles in unit volume.

In what follows we are concerned specially with values of p in the neighbourhood of a frequency p_s. We shall assume that the region of absorption in question is removed from other similar regions, so that in the above summation all the terms except one may be replaced by a quantity independent of p; hence, in the vicinity of a frequency p_1, we write

$$\frac{1}{\sigma+1/(\mathfrak{n}^2-1)} = q_1 + \frac{C_1}{p_1^2-p^2+ib_1p}. \tag{2}$$

Solving for n^2, and separating real and imaginary parts, we find

$$n^2(1-\kappa^2) = q_1' + \frac{C_1'(p_1'^2-p^2)}{(p_1'^2-p^2)^2+b_1^2p^2}; \quad 2n^2\kappa = \frac{C_1'b_1p}{(p_1'^2-p^2)^2+b_1^2p^2};$$

$$q_1' = \frac{1+q_1(1-\sigma)}{1-q_1\sigma}; \quad C_1' = \frac{C_1}{(1-q_1\sigma)^2}; \quad p_1'^2 = p_1^2 - \frac{C_1\sigma}{1-q_1\sigma}. \tag{3}$$

We make the following substitutions:—

$$x^2 = \frac{q_1'}{C_1'}p^2; \quad x'^2 = \frac{q_1'}{C_1'}p_1'^2; \quad b^2 = \frac{q_1'}{C_1'}b_1^2;$$

$$\alpha = x^2 - x'^2; \quad \beta = bx. \tag{4}$$

The previous expressions reduce to

$$\frac{n^2(1-\kappa^2)}{q_1'} = 1 - \frac{\alpha}{\alpha^2+\beta^2}; \quad \frac{2n^2\kappa}{q_1'} = \frac{\beta}{\alpha^2+\beta^2}. \tag{5}$$

Equations of this form, with q_1' unity and with different variables, have been investigated by various writers; in studying the extinction curve of $n\kappa$ as a function of wave-length approximate methods have been used. For example, Planck* makes three types according as the maximum of $n\kappa$ is a large, medium, or small number. The last case is the usual approximation which treats β as a large number, the result being a curve for $n\kappa$ symmetrical on both sides of a maximum which occurs near a frequency given by $\alpha = 0$. In the first case, when $n\kappa$ is large, Planck illustrates the unsymmetrical nature of the curve, and after various assumptions, states that its maximum is given by $\beta = \alpha\sqrt{3}$.

Königsberger and Kilching† also point out that the maximum of $n\kappa$ does not occur at the frequency p_1' of the present notation; as a result of an experimental study they conclude that in strongly absorbing substances, in the visible spectrum, the maximum of $n\kappa$ is about $10\,\mu\mu$ from λ_1' towards the shorter wave-lengths. They state that no formula has been derived for the position of the maximum, on account of the complexity of the equations involved.

Without limiting the values of the coefficients we can proceed in the following manner. Solving the equations (5) we have

$$\frac{2n^2}{q_1'} = \left\{1+\frac{1-2\alpha}{\alpha^2+\beta^2}\right\}^{\frac{1}{2}} + 1 - \frac{\alpha}{\alpha^2+\beta^2};$$

$$\frac{2n^2\kappa^2}{q_1'} = \left\{1+\frac{1-2\alpha}{\alpha^2+\beta^2}\right\}^{\frac{1}{2}} - 1 + \frac{\alpha}{\alpha^2+\beta^2};$$

$$\kappa = \frac{\{(\alpha^2+\beta^2-\alpha)^2+\beta^2\}^{\frac{1}{2}} - (\alpha^2+\beta^2-\alpha)}{\beta}. \tag{6}$$

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* M. Planck, 'Sitzungsber. Akad. Berlin,' 1903, vol. 1, p. 480.

† Königsberger and Kilching, 'Ann. der Physik,' 1909, vol. 28, p. 889; also 1910, vol. 32, p. 843.

We see that the maximum of κ occurs when $(\alpha^2+\beta^2-\alpha)/\beta$ has its maximum; that is, when

$$\beta(2\alpha-1)\,d\alpha-(\alpha^2-\beta^2-\alpha)\,d\beta=0,$$

$$3\alpha^2+(4x'^2+b^2-1)\,\alpha+(b^2-2)\,x'^2=0.$$

We shall find it convenient to write

$$g=\frac{1}{x'^2};\quad k=\frac{b}{x'};\quad y=\frac{\alpha}{x'^2}=\frac{x^2-x'^2}{x'^2}=\frac{p^2-p_1'^2}{p_1'^2}=\frac{\lambda_1'^2-\lambda^2}{\lambda^2}.$$

The equation for the maximum of κ becomes

$$3y^2+(4+k^2-g)\,y+(k^2-2g)=0. \tag{7}$$

The only root which comes into consideration is

$$y_\kappa=\tfrac{1}{6}\left[\{(4+k^2-g)^2+12\,(2g-k^2)\}^{\frac{1}{2}}-(4+k^2-g)\right], \tag{8}$$

We shall find that k is small compared with g; if in addition g is small we have often a sufficient approximation in

$$y_\kappa=\tfrac{1}{2}g. \tag{9}$$

For the maximum of $n\kappa$ we differentiate the expression

$$\{1+(1-2\alpha)/(\alpha^2+\beta^2)\}^{\frac{1}{2}}+\alpha/(\alpha^2+\beta^2).$$

Expressing β, $d\alpha$, and $d\beta$ in terms of α and rationalising the equation, we find eventually a quartic equation in α,

$$\begin{aligned}12\alpha^4+(16x'^2+4b^2-8)\,\alpha^3-(12x'^2+8b^2x'^2+5b^2)\,\alpha^2\\-(16b^2x'^4+4b^2x'^2+4b^4x'^2+b^4)\,\alpha+(4x'^2-b^2-4b^2x'^2)\,b^2x'^2=0.\end{aligned} \tag{10}$$

With values of b and x' such as occur in practice, the coefficients in brackets in this equation are all positive. The equation has extraneous roots which have entered in rationalising the equation for a maximum of $n\kappa$; it is easily seen that it is the smaller positive root which corresponds to a maximum of $n\kappa$. With the same notation as before, the equation becomes

$$\begin{aligned}12y^4+(16+4k^2-8g)\,y^3-(12g+8k^2+5gk^2)\,y^2\\-(4+g)\,(4+k^2)\,k^2y+\{4g-(4+g)\,k^2\}\,k^2=0.\end{aligned} \tag{11}$$

We can see what the other roots of this equation signify by finding the positions of maximum and minimum refractive index; for this we proceed in the same manner by differentiating

$$\frac{2n^2}{q_1'}=\left(1+\frac{g^2-2gy}{y^2+k^2y+k^2}\right)^{\frac{1}{2}}+1-\frac{gy}{y^2+k^2y+k^2}.$$

After some reduction, one obtains again the same equation (11). The equation has, in practice, four real roots, two positive and two negative. One of the negative roots is clearly greater than 1 numerically; remembering that y is $(\lambda_1'^2-\lambda^2)/\lambda^2$, we see that this root does not enter into consideration. For the other three roots we find the following correspondence:—

Larger positive root (y_n)	Minimum of n,
Smaller positive root ($y_{n\kappa}$)	Maximum of $n\kappa$,
Negative root, numerically <1, ($y_{n'}$)	Maximum of n.

For a first approximation for the smaller roots one can write, as the more important terms of the equation,

$$12gy^2+4k^2(4+g)\,y-4gk^2=0.$$

Hence, approximately,

$$y=\frac{1}{6g}[\pm\{(4+g)^2k^4+12g^2k^2\}^{\frac{1}{2}}-(4+g)\,k^2]. \tag{12}$$

Taking the radicle with the positive sign, we have $y_{n\kappa}$; while with the negative sign we obtain $y_{n'}$.

For the larger positive root we have approximately

$$12y^4+(16-8g)\,y^3-12gy^2=0,$$

$$y_n=\tfrac{1}{3}[\{(2-g)^2+9g\}^{\frac{1}{2}}-(2-g)]. \tag{13}$$

Of these approximations, that for $y_{n\kappa}$ is generally very good; the others give at least the first significant figure, and one can then obtain the roots from the complete quartic to any desired accuracy.

For the reflective power R we have

$$\mathrm{R}=\frac{(n-1)^2+n^2\kappa^2}{(n+1)^2+n^2\kappa^2}.$$

R is a maximum when $2n/(n^2+n^2\kappa^2+1)$ is a minimum, that is when

$$(n^2-n^2\kappa^2-1)\,dn+2n^2\kappa d\,(n\kappa)=0,$$

or

$$(n^2+n^2\kappa^2+1)\,dn+2n^3\kappa d\kappa=0. \tag{14}$$

The procedure of the two previous cases leads to an equation which is much too complicated to be of service; in the examples which follow, the maximum of R is found by graphing its values when calculated from the formula. If κ were zero, R (max.) would occur at n (max.). From the above equations, if the absorption is small or n is large, so that $n^2\kappa^2<n^2-1$, R (max.) could occur between n (max.) and $n\kappa$ (max.); otherwise the maximum of R comes between the maxima of κ and $n\kappa$.

For comparison with other formulæ and with experimental data, it is convenient to change from frequency to wave-length.

From (5) we obtain

$$\frac{n^2(1-\kappa^2)}{q_1'}=1+\frac{g\lambda^2(\lambda^2-\lambda_1'^2)}{(\lambda^2-\lambda_1'^2)^2+g'^2\lambda^2}; \qquad \frac{2n^2\kappa}{q_1'}=\frac{gg'\lambda^3}{(\lambda^2-\lambda_1'^2)^2+g'^2\lambda^2}; \tag{15}$$

where $k = g'/\lambda_1'$, and g and k are the quantities already used in the equations for the maxima.

We may bring together the various wave-lengths which are to be compared. Suppose the dispersion formula is in the form (2), or

$$\frac{1}{\sigma+1/(n^2-1)} = q_1 + \frac{C_1\lambda_1^2\lambda^2/4\pi^2c^2}{\lambda^2-\lambda_1^2+ib_1\lambda_1^2\lambda/2\pi c}. \tag{16}$$

Then λ_1 is the wave-length of the natural undamped vibrations of a single particle if isolated. λ_1' is an associated wave-length for the medium as a whole, and is the limiting position of maximum absorption when κ is small and the region of absorption is narrow. λ_1' is greater than λ_1, and $\lambda_1'^2$ is equal to $\lambda_1^2\{1-C_1\lambda_1^2\sigma/4\pi^2c^2(1-q_1\sigma))^{-1}$.

We have, further, the actual maximum of $n\kappa$, which is displaced towards the shorter wave-lengths from λ_1' and is given by $\lambda_1'(1+y_{n\kappa})^{-\frac{1}{2}}$ in the present notation; similarly we have the maximum of κ and of the reflective power.

It is of interest incidentally to express some of the constants in the manner of Drude, considering the natural vibrations as due to a particle of mass m, charge e; N being the number of such particles per unit volume, and p the number per molecule of the substance.

In (16) above we have $C_1\lambda_1^2/4\pi^2c^2 = 4\pi Ne^2/m$. The equation (16), neglecting absorption, transforms to

$$n^2 = q_1' + \frac{C_1'\lambda_1'^2\lambda^2/4\pi^2c^2}{\lambda^2-\lambda_1'^2},$$

where q_1' and C_1' are given by (3). Hence we have

$$\frac{g}{\lambda_1'^2} = \frac{C_1'}{4\pi c^2 q_1'} = \frac{C_1\{1+\sigma(q_1'-1)\}^2}{4\pi^2c^2q_1'} = \frac{1}{\pi}\,\frac{Ne^2/c^2}{m}\,\frac{\{1+\sigma(q_1'-1)\}^2}{q_1'}.$$

Expressing e in electromagnetic units, and with M for the molecular weight and d for the density of the substance, also with 9660 as the value of e/m for hydrogen, we obtain

$$p\frac{e}{m} = \frac{\pi}{9660}\,\frac{M}{d}\,\frac{g}{\lambda_1'^2}\,\frac{q_1'}{\{1+\sigma(q_1'-1)\}^2}. \tag{17}$$

Simpler forms which have been used are found by putting σ zero, or by writing q_1' equal to unity.

Iodeosin.

Königsberger and Kilching (*loc. cit.*) have made recently a quantitative study of various strongly absorbing media. It is sufficient to take one example, iodeosin, for which they give the values of n and $n\kappa$ throughout a region of absorption in the visible spectrum; they estimate that this region is associated with one vibrating electron per molecule. We take the values of g, g' and λ_1' which they have calculated from their results, namely,

$$\lambda_1' = 5{\cdot}21 \times 10^{-5}\,\text{cm.}; \quad g = 0{\cdot}257; \quad g' = 6{\cdot}47 \times 10^{-6}; \quad k = g'/\lambda_1' = 0{\cdot}12418.$$

From the observed values it is seen that the maximum of $n\kappa$ is 0·82 and occurs at 510 $\mu\mu$. The minimum and maximum of n are at 480 $\mu\mu$ and 550 $\mu\mu$ respectively. The maximum of κ is at about 495 $\mu\mu$; and by calculating and graphing the reflective power, we find its maximum is 18 per cent. at rather less than 540 $\mu\mu$. From equation (8) we have $y_\kappa = 0{\cdot}0963$, and this gives 497 $\mu\mu$ as the maximum of κ. The equation (11) becomes

$$12y^4 + 14{\cdot}006y^3 - 3{\cdot}227y^2 - 0{\cdot}2636y + 0{\cdot}01484 = 0.$$

The approximations of (12) and (13) give for the three roots we need, $-0{\cdot}1$, $0{\cdot}041$, $0{\cdot}2$. From the quartic equation one has more accurately the values $-0{\cdot}095$, $0{\cdot}0412$, $0{\cdot}24$. For the minimum and maximum of n these give 468 and 548 $\mu\mu$ respectively; and for the maximum of $n\kappa$ we find 510 $\mu\mu$.

These calculations agree well with the observed values, except for the minimum of n; of course from the method of calculation in this case any considerable lack of agreement is due to n and $n\kappa$ not being represented with sufficient accuracy by simple dispersion formulæ with the above values of the constants. Using a Lorentz type of formula, Königsberger and Kilching calculate λ_1 for the natural undamped vibrations as 497 $\mu\mu$. We have then the following series of wave-lengths :—

λ_1 and λ_κ.	$\lambda_{n\kappa}$.	λ_1'.	λ_R.
497	510	520	540

We notice that $\lambda_R > \lambda_1'$ in this case, corresponding with the fact that in this region $n^2\kappa^2 < n^2 - 1$, as in equation (14).

Carbon Disulphide.

We consider now a substance for which quantitative measurements of the selective absorption are not available; we confine our attention to the principal region in the ultra-violet. In a previous paper various dispersion formulæ for CS_2 were examined; using values of the refractive index given by Flatow, namely :—

λ	441	508	589
n	1·67180	1·64586	1·62806,

one obtained a formula,

$$\frac{n^2-1}{n^2+2} = q + \frac{C}{\lambda^2 - \lambda_1^2}, \tag{18}$$

with

$$q = 0{\cdot}33567; \quad C = 0{\cdot}005843; \quad \lambda_1^2 = 0{\cdot}04338; \quad \lambda_1 = 208\,\mu\mu$$

This is not given as a complete formula; it ignores, for example, the minor region of absorption near 325 $\mu\mu$, but it suffices for the present purpose. We have to introduce a suitable value for g', denoting absorption, and then work out the various maxima. In order to do this, we first transform (18) to the form

$$\frac{n^2}{q_1'} = 1+\frac{g\lambda^2}{\lambda^2-\lambda_1'^2}, \tag{19}$$

so that we can compare it with the complete formulæ in (15). Making the calculations we find

$q_1' = 1{\cdot}7544$; $g = 0{\cdot}434$; $\lambda_1'^2 = 5{\cdot}217\times 10^{-10}$; $\lambda_1' = 2{\cdot}284\times 10^{-5}$ cm.

From (17), with σ equal to $\frac{1}{3}$, we have

$$p\frac{e}{m} = \frac{\pi}{9660}\,\frac{\mathrm{M}}{d}\,\frac{g}{\lambda_1'^2}\,\frac{9q_1'}{(q_1'+2)^2} = 1{\cdot}79\times 10^7.$$

This indicates one electron per molecule, in contrast with Drude's calculation, which gave two electrons per molecule. In Drude's form σ is zero; if we write $n^2 = \Sigma m'\lambda^2/(\lambda^2-\lambda'^2)$ and use Flatow's values of m' and λ' for CS_2 at 20°, we have

$$p\frac{e}{m} = \frac{\pi}{9660}\,\frac{\mathrm{M}}{d}\,\frac{m'}{\lambda'^2} = 2\times 1{\cdot}53\times 10^7.$$

We have now to introduce a suitable value of g', so that (19) is replaced by the two equations (15). A simple way would be available if we knew the reflective power R at λ_1'; for at this place we have $n^2(1-\kappa^2) = q_1'$ and $2n^2\kappa = q_1'g\lambda_1'/g' = q_1'g/k$.

Another method would be to use a knowledge of the position of any of the maxima, for the quartic equation (11) in y is a quadratic for k. In the present case we adopt another method. Retaining the above values of q_1', g and λ_1' unaltered, for simplicity, means that we regard κ as inappreciable at the wave-lengths at which these constants were determined. Now the index n is given by Flatow as 2·08884 at a wave-length 267 $\mu\mu$. The formula (19) gives a calculated value much too high, and by trial we estimate g' so as to reduce this value nearer to the observed one at 267, without having much effect at 441 $\mu\mu$.

It is sufficient to take $g' = 2{\cdot}284\times 10^{-6}$, that is $k = 0{\cdot}1$; we obtain then a calculated index of 2·0904 at 267 $\mu\mu$. This value of g' is probably of the right order of magnitude, and we proceed with the constants of (15) so determined.

For the maximum of κ we find $y_\kappa = 0{\cdot}205$, and $\lambda_\kappa = 208\,\mu\mu$. We have also $\lambda' = 208\,\mu\mu$; in this case, as in the previous one, the maximum of κ coincides practically with the wave-length λ_1. The quartic equation becomes

$$12y^4+12{\cdot}568y^3-5{\cdot}3097y^2-0{\cdot}1778y+0{\cdot}01693 = 0.$$

The roots required are $-0{\cdot}066$, $0{\cdot}044$, and $0{\cdot}34$. Hence $\lambda_{n\kappa}$ is 223·4 $\mu\mu$; and the minimum and maximum of n are at 198 and 236·4 respectively. In fig. 1 the values of n and $n\kappa$ have been graphed from the formulæ: one notices the unsymmetrical nature of the curves, $n\kappa$ descending more steeply towards the longer wave-lengths, and the maximum of n being sharper than the minimum. From the calculated values one obtains the curve of reflective power R; its maximum is about 40 per cent. at 215 $\mu\mu$, a smaller wave-length than for the maximum of $n\kappa$. The only experimental result available in this respect is an observation by Flatow. Using a method of repeated reflection from carbon disulphide pressed between plates of quartz or fluorspar, he concluded that the maximum of selective reflection was in the vicinity of 230 $\mu\mu$. One might apply certain corrections allowing for the presence of the quartz plate, for instance, by using the relative index of refraction; but any such correction would tend to increase slightly the above estimate. Possibly the absorption coefficients are too large in the formulæ we have used; but in any case further observations by means of residual rays in the ultra-violet are desirable.

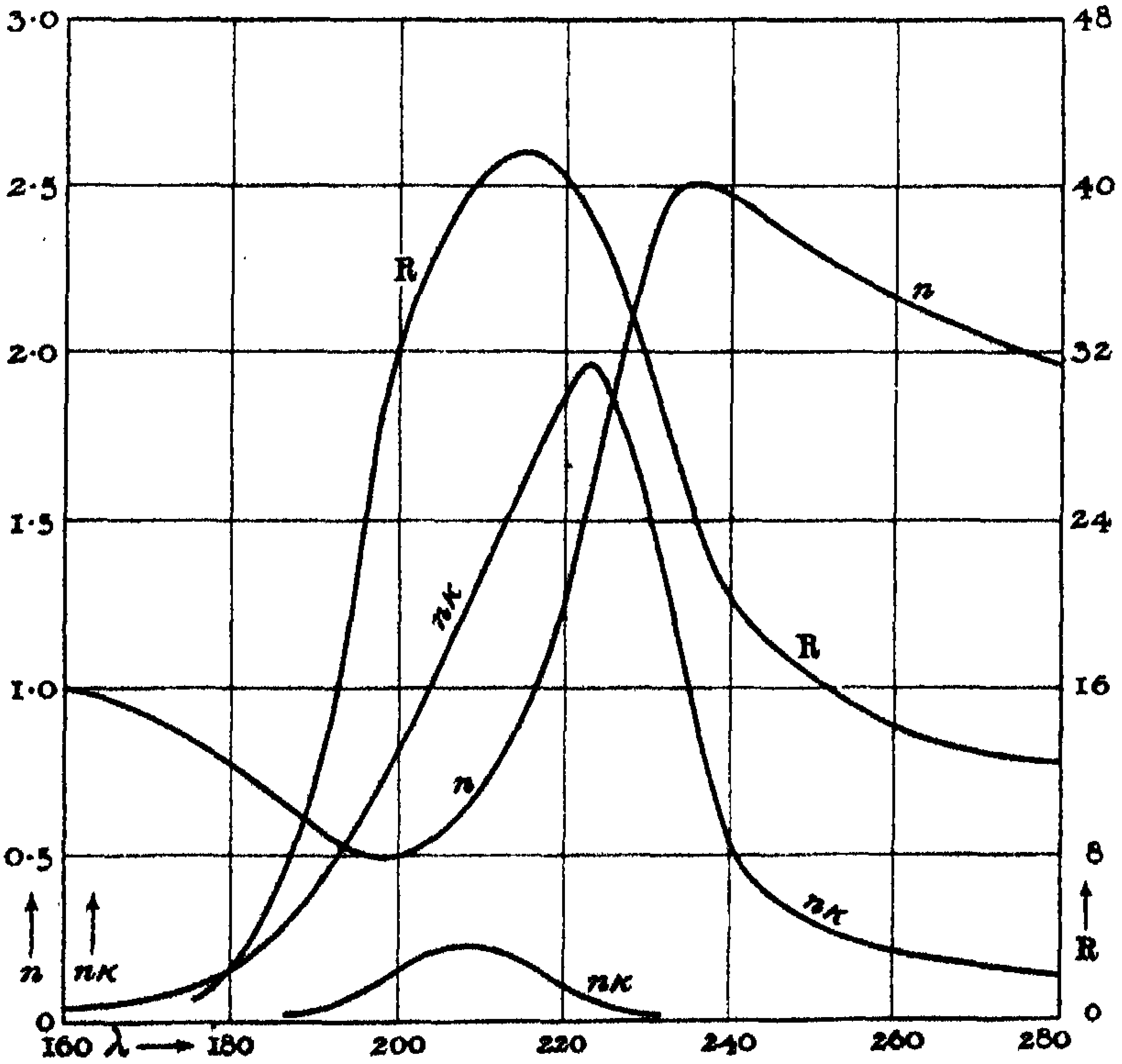

Fig. 1.

There is more satisfactory agreement in the case of the absorption maximum. The observations refer to a capillary layer of a solution of one part by volume of carbon disulphide in ten parts of alcohol; it was found that almost complete absorption occurred from about 190 to 228 $\mu\mu$, with a mean position of 210 $\mu\mu$.

We must modify the constants so as to make the formulæ suitable for such a solution. This problem deserves fuller investigation, but for the present we use the following method of estimating the effect. We assume that $(n^2-1)/(n^2+2)$ is additive, so that, for volumes V_1 and V_2 of two substances making a total volume V of solution, we have

$$\frac{n^2-1}{n^2+2} = \frac{V_1}{V}\frac{n_1^2-1}{n_1^2+2} + \frac{V_2}{V}\frac{n_2^2-1}{n_2^2+2}.$$

Instead of equation (18) we have a similar one with different constants, the transformation to the form (19) giving the scheme

$$n^2(1-\kappa^2) = q_2 + \frac{C_2\lambda^2(\lambda^2-\lambda_1'^2)}{(\lambda^2-\lambda_1'^2)^2+g'^2\lambda^2}; \qquad 2n^2\kappa = \frac{C_2 g'\lambda^3}{(\lambda^2-\lambda_1'^2)^2+g'^2\lambda^2};$$

$$q_2 = q_1' - C_1'/\lambda_1'^2; \quad C_2 = C_1'/\lambda_1'^2; \quad q_1' = (1+2q_1)/(1-q_1);$$

$$C_1' = 3C_1/(1-q_1)^2; \quad \lambda_1'^2 = \lambda_1^2 + C_1/(1-q_1); \quad C_1 = V_1C/V;$$

$$q_1 = \frac{V_1}{V}q + \frac{V_2}{V}\frac{n_2^2-1}{n_2^2+2}. \tag{20}$$

In the present case we may ignore any absorption due to the solvent, and also assume n_2 as constant (1·43) in the range in question.

For the dissolved substance we take the values of q, C, and λ_1 the same as before, in (18); taking the volumes in the ratio of 1 to 10, we find the values

$$\lambda_1' = 210\,\mu\mu; \quad q_2 = 2{\cdot}016; \quad g = C_2/q_2 = 0{\cdot}033.$$

If we give k the same value as before, we have $k = 0{\cdot}1$ and $g' = 2{\cdot}1\,.\,10^{-6}$. From equation (12) we find $y_{n\kappa} = 0{\cdot}008$ and consequently the maximum of $n\kappa$ is at the wave-length 209 $\mu\mu$. This agrees well with the observed mean position of 210 $\mu\mu$ for the solution. The curve for $n\kappa$ for the solution has been graphed and is shown in fig. 1.

Rock Salt.

For this substance we consider first Maclaurin's dispersion formula,*

$$\frac{n^2-1}{n^2+a} = \frac{K-1}{K+a} + \frac{C_1}{\lambda^2-\lambda_1^2} + \frac{C_2}{\lambda^2-\lambda_2^2},$$

$$\begin{array}{ll} \lambda_1^2 = 0{\cdot}0160074, & \lambda_2^2 = 2632{\cdot}14, \\ C_1 = 0{\cdot}00191605, & C_2 = 683{\cdot}816, \\ a = 5{\cdot}51, & K = 5{\cdot}9, \\ \lambda_1 = 0{\cdot}12652\,\mu. & \lambda_2 = 51{\cdot}3\,\mu. \end{array}$$

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* 'Roy. Soc. Proc.,' A, 1908, vol. 81, p. 367.

For this form, with a general instead of equal to 2, we can easily modify the previous expressions for reduction to the required form. We find in the vicinity of λ_1, with the same notation as in (19),

$$q_1' = 1{\cdot}3422; \quad g = 0{\cdot}7359; \quad \lambda_1' = 0{\cdot}1353\,\mu.$$

For the value of $p.e/m$ from (17) we have $M = 58{\cdot}5$, $d = 2{\cdot}28$, and $\sigma = 1/6{\cdot}51$; we find $p.e/m = 4{\cdot}06 \times 10^7$. This might be interpreted as two electrons per molecule. Drude's calculation gave a value of $4 \times 1{\cdot}57 \times 10^7$.

To estimate the maximum of $n\kappa$ we take $k = 0{\cdot}1$, so that $g' = 1{\cdot}353\,.\,10^{-6}$. We obtain $y_{n\kappa} = 0{\cdot}048$, and the maximum of $n\kappa$ occurs at $0{\cdot}1322\,\mu$. The reflective power has not been calculated in this case; apart from this we have the sequence $\lambda_1 = 0{\cdot}1265\,\mu$, $\lambda_{n\kappa} = 0{\cdot}1322\,\mu$, and $\lambda_1' = 0{\cdot}1353\,\mu$.

We consider now more fully the region in the infra-red. Making similar calculations, we find

$$q_2' = 2{\cdot}332; \quad g = 1{\cdot}53; \quad \lambda_2 = 513 \times 10^{-5}\,\text{cm.}; \quad \lambda_2' = 619 \times 10^{-5}\,\text{cm.}$$

If we calculate pe/m in this case we find a value 536, indicating a vibrating particle of mass comparable with that of the molecule, if we hold to the simple interpretation.

We have no direct guide to an estimate of g'. We keep to the previous method of putting $k = g'/\lambda_2' = 0{\cdot}1$; we shall find that this gives values of the reflective power similar to those obtained by experiment. Reverting to the primitive form of the dispersion formula in (1), it appears that making k constant is equivalent to making the quantity b_1 vary directly as the natural frequency; b_1 appears in the equation of the vibrating particle in the term $b_1 dx/dt$, a term which is frequently written in the form $b_1 p_1 dx/dt$.

Having assigned the values of the constants, we calculate the various maxima. We find $y_\kappa = 0{\cdot}676$ and $\lambda_\kappa = 47{\cdot}8\,\mu$.

The quartic equation becomes

$$12y^4 + 3{\cdot}8y^3 - 18{\cdot}516y^2 - 0{\cdot}2217y + 0{\cdot}06065 = 0.$$

The required roots are 0·052, 1·09, and −0·063. These give $\lambda_{n\kappa} = 60{\cdot}3\,\mu$, and the minimum and maximum of n at $42{\cdot}8\,\mu$ and $63{\cdot}9\,\mu$ respectively.

Values of n and $n\kappa$ have been calculated and the curves are shown in fig. 2; on account of the larger magnitudes the unsymmetrical features are very marked. The values of the reflective power R have also been graphed; we find a maximum of about 76 per cent. at $52\,\mu$. Recent experiments with residual rays give a double maximum with a mean position of $52{\cdot}3\,\mu$. Other observations have given the following estimated values of R in percentages:—1·7 at $23{\cdot}7\,\mu$, 81·5 at $51{\cdot}2\,\mu$, 52·6 at $61{\cdot}1\,\mu$, 25·8 at $82{\cdot}3\,\mu$, and 20·3 at 108 μ; these have been marked by circles in fig. 2, and one sees that the calculated curves agree well in a general way with these results. Probably the value of g' is too large, and one might obtain a less rounded curve by taking a smaller value, but one does not lay much stress on actual agreement, because the curves are meant to be illustrative in the first instance.

With the above formula, Maclaurin identified λ_2 with the position of maximum reflection obtained by residual rays, taking that to be 51·3 μ. We have seen that, compared with the simpler form of dispersion formula, the wave-length λ_1 is replaced by λ_1', equal to 61·9 μ, which would be the position of maximum absorption if that were small. Putting in a more suitable value for the absorption, we have found that the maximum is at 60·3 μ, only slightly displaced to the shorter wave-length from λ_1'; however, under the same conditions we find that the maximum of selective reflection occurs at 52 μ.

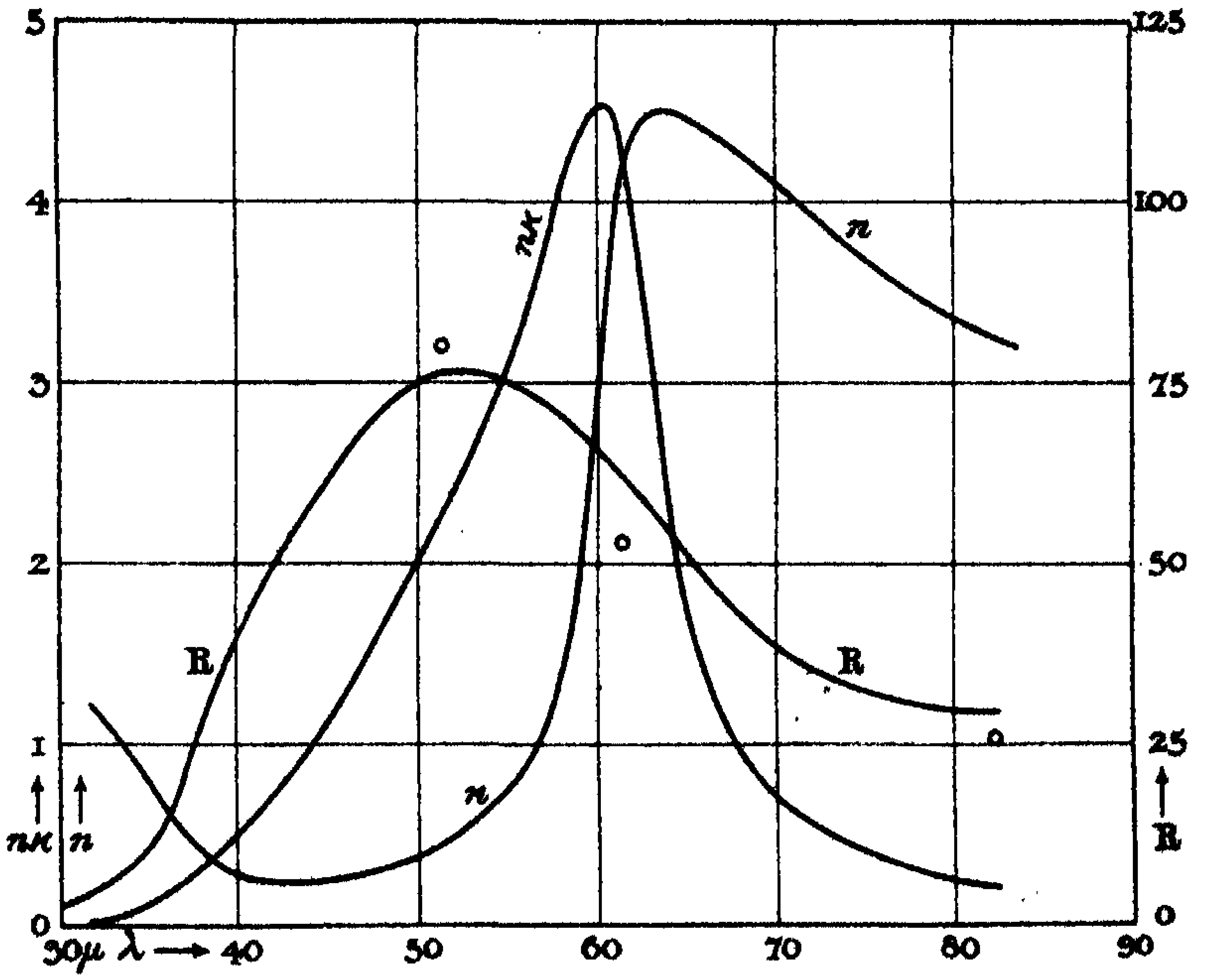

FIG. 2.

Similar calculations could be made for any of the dispersion formulæ which have been given for rock salt. These are generally in the form $n^2-1 = \Sigma C_1/(\lambda^2-\lambda_1^2)$, that is, σ is zero and λ_1' coincides with λ_1. Martens in making such a formula put the wave-length λ_r for the infra-red equal to the observed position of maximum reflection, but we have seen that when absorption coefficients are introduced the maximum of R occurs at a considerably less wave-length than the λ_r of the formula. Paschen[*] determined λ_r directly from the values of the refractive index, and claims that his formula with $\lambda_r = 60\mu$ represents the dispersion better, in spite of apparent disagreement with the reflection maximum. If we put Paschen's formula into the form used above, for the vicinity of $60\,\mu$, we find $q_2' = 2{\cdot}33$, $g = 1{\cdot}44$, and $\lambda_2' = 60\,\mu$. These values are not much different from those of Maclaurin's formula when expressed similarly. It is unnecessary to repeat the calculations; if we introduced a quantity g' as before, we should find the maximum of reflective power to be in the neighbourhood of $50\,\mu$. It seems probable then that Paschen's formula, when interpreted aright, does not disagree with the results of reflection experiments.

Absorption in Vapours.

The absorption in the previous cases is enormously larger than that of gases and vapours, so that the differences between the various maxima in the latter are very minute and generally quite beyond the limits of observation. For dense mercury vapour R. W. Wood[†] has been able to observe selective reflection, with the interesting result that the maximum reflective power occurs at about one Ångström unit towards the shorter wave-lengths from the absorption maximum. The particular line in question is near 2536 Å.U., and it shows powerful anomalous dispersion. The vapour was contained in a fused quartz tube, and Wood suggests that the displacement is entirely a spurious effect due to the relative index of refraction of quartz and the vapour being nearly unity on the side of the longer wave-lengths but quite large towards the shorter wave-lengths from the absorption line. There are no data available for the dispersion of mercury vapour by which one might test this numerically. As a similar example we use the values given by Wood for dense sodium vapour; for a single mean absorption at 5893 Å.U., the dispersion formula is

$$n^2 = 1 + \frac{g\lambda^2}{\lambda^2 - \lambda_1^2},$$

with $$g = 5{\cdot}5 \times 10^{-5}, \quad \lambda_1 = 5{\cdot}893 \times 10^{-5}\,\text{cm}.$$

This formula is only approximate; to obtain any approach to observed values near the D-lines, Wood alters the value of λ_1. However, one can use it as an example of the numerical magnitudes of the quantities. It has been estimated that in less dense sodium vapour the logarithmic decrement of the natural vibrations is of the order 10^{-5}; in the present case we shall take $k = g'/\lambda_1 = 4 \times 10^{-5}$, a value which gives moderate reflective powers. From the formula (12) we find that the maximum of $n\kappa$ is at less than 5893 by about 0·014 Å.U. Working out values of n and $n\kappa$ we obtain a maximum reflective power of 9·6 per cent. at 5892·9 Å.U. If we divide the values of n by a mean value for the index of quartz, say 1·55, we can graph the reflective power taking account of the effect of the wall of the tube; this shifts the maximum further to the shorter wave-lengths by about 0·1 Å.U. We obtain thus a total displacement of about 0·2 Å.U., of which one-half is due to the wall of the tube. This displacement is several times smaller than that observed in mercury vapour, but there are certain possibilities to be noticed. In sodium vapour with the above value of g it has been estimated that there is not more than one vibrating electron for every 12 molecules; in mercury vapour the ultra-violet line showed very strong anomalous dispersion, and is probably a more dominant natural vibration with a larger value of g. In addition, the absorption extended over several Ångström units. Hence the conclusion is that while the displacement observed by Wood may be exaggerated by the presence of the quartz wall, it is probably in part a true effect—a displacement of the reflection maximum from the absorption maximum towards the shorter wave-lengths.

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[*] F. Paschen, 'Ann. der Physik,' 26, p. 130, 1908.

[†] R. W. Wood, 'Phil. Mag.,' 18, p. 187, 1909.

The Influence of the Solvent on the Position of Absorption Bands in Solutions.

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1. The absorption spectra of solutions of the same substance differ according to the nature of the solvent, the absorption bands varying in position and in character. An attempt was made by Kundt[*] to reduce the variations to order by a rule which was based on experiment; he concluded that the effect of the solvent was to displace the absorption bands further towards the longer wave-lengths, the greater the refractive or dispersive power of the solvent. If this rule had proved sufficient, one might have inferred that the molecules of the dissolved substance move about in the solvent without any essential change in constitution. Further experiments have shown that the problem is by no means so simple; although Kundt's rule expresses a true effect, there is also the influence, often more important, of physical or chemical molecular changes such as are expressed by the terms association, dissociation, and solvation. Even apart from these complications, the matter does not appear to have been considered theoretically to any extent. It seems desirable to supply a definite formulation of Kundt's rule, such as can be obtained by using a suitable type of dispersion formula; one may then attempt in some cases a numerical estimate of the effects which can be ascribed to its operation.

2. The Sellmeier type of formula, in which $n^2-1 = \Sigma c_1/(\lambda^2-\lambda_1^2)$, is not sufficiently elastic to include the effect of the solvent. For a region of selective absorption, the maximum occurs near λ_1, the upper limit of the range of wave-lengths for which n^2 is negative; λ_1 is also the wave-length of the natural vibrations, and is presumably a molecular quantity independent of the surrounding medium. The only method with this type of formula would be to assert a direct change in the free molecular periods, a remark which applies also to the effect of change of density as well as of refractive index of the medium. On the other hand, for a dispersion formula with $1/\{\sigma+1/(n^2-1)\}$ in place of n^2-1, a maximum of absorption is near a wave-length λ_1', which differs from λ_1 by an amount involving the constants of the formula; in other words, the position of maximum absorption is dependent upon the density and optical nature of the medium. This holds

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[*] A. Kundt, 'Ann. der Physik,' 1878, vol. 4, p. 34.

true with any constant value of σ, provided it is not zero. We shall find it sufficient here to use the form with σ equal to $\frac{1}{3}$, only noting the possibility of further refinements. We have now to estimate the change of position of an absorption band when the absorbing particles are immersed in differently refracting media.

3. Let n, P, D, be the refractive index, weight, and density of a mixture of weights p_1 and p_2 of two substances whose indices and densities are n_1, d_1, and n_2, d_2, respectively. In regions free from absorption, a simple law of mixtures has been proved capable of expressing the results of experiment,* namely,

$$\frac{\mathrm{P}}{\mathrm{D}}\frac{n^2-1}{n^2+2} = \frac{p_1}{d_1}\frac{n_1^2-1}{n_1^2+2}+\frac{p_2}{d_2}\frac{n_2^2-1}{n_2^2+2}. \qquad (1)$$

In regions of anomalous dispersion there is not so much evidence, but one instance is the calculation of Hurion† from a similar formula for a solution of iodine in carbon disulphide; he deduced values of the refractive index of iodine which agree well with those obtained since by direct measurement. We assume, then, that the same law of mixtures holds near a region of selective absorption, and we simplify the calculations by supposing that near such a region for the dissolved substance (n_1) the solvent (n_2) has normal slight dispersion. We further suppose that in this region for the salt we have, with sufficient accuracy,

$$\frac{n_1^2-1}{n_1^2+2} = q_1+\frac{\mathrm{C}_1}{\lambda^2-\lambda_1^2}. \qquad (2)$$

From this formula, for the undiluted absorbing salt, the wave-length λ_1' is equal to $\{\lambda_1^2+\mathrm{C}_1/(1-q_1)\}^{\frac{1}{2}}$. To obtain the actual maximum of absorption one must complete (2) by including terms denoting true absorption; for an investigation one may refer to a previous paper,‡ where it is shown that the maximum occurs at a wave-length rather less than λ_1', but this difference is only appreciable for strong absorption.

For the solution we have from (1)

$$\frac{\mathrm{P}}{\mathrm{D}}\frac{n^2-1}{n^2+2} = \frac{p_1}{d_1}q_1+\frac{p_2}{d_2}\frac{n_2^2-1}{n_2^2+2}+\frac{p_1\mathrm{C}_1/d_1}{\lambda^2-\lambda_1^2}. \qquad (3)$$

It is sufficient for the present purpose to make n_2 constant at its value in the neighbourhood of λ_1. Equation (2) can be reduced to

$$n^2 = q_1'+\frac{\mathrm{C}_1'\lambda^2}{\lambda^2-\lambda_1'^2};$$

$$q_1' = \frac{1+2q_1}{1-q_1}; \qquad \mathrm{C}_1' = \frac{3\mathrm{C}_1}{(1-q_1)^2}; \qquad \lambda_1'^2 = \lambda_1^2+\frac{\mathrm{C}_1}{1-q_1}. \qquad (4)$$

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* *Cf.* C. Chéveneau, 'Ann. de Chim. et de Phys.,' 1907, vol. 12, p. 145.

† Hurion, 'Ann. de l'École Norm.,' 1878, vol. 6, p. 367.

‡ 'Roy. Soc. Proc.,' A, this volume, p. 1.

We have a similar transformation for (3), in which for q_1 we write $\frac{D}{P}\left(\frac{p_1}{d_1}q_1+\frac{p_2}{d_2}\frac{n_2^2-1}{n_2^2+2}\right)$, and for C_1 we put $\frac{p_1C_1}{d_1}\frac{D}{P}$.

Writing q_2 for $(n_2^2-1)/(n_2^2+2)$, we have for the solution under the limitations which have been specified

$$\lambda_1'^2-\lambda_1^2 = \frac{p_1C_1/d_1}{\frac{P}{D}-\frac{p_1}{d_1}q_1-\frac{p_2}{d_2}q_2}; \qquad C_1' = \frac{3Pp_1C_1/Dd_1}{\left(\frac{P}{D}-\frac{p_1}{d_1}q_1-\frac{p_2}{d_2}q_2\right)^2}. \tag{5}$$

As a general result we can see that λ_1' moves further to the longer wave-lengths from λ_1, according as the solvent increases the quantity $\frac{P}{D}-\frac{p_1}{d_1}q_1-\frac{p_2}{d_2}q_2$; further, since the intensity of the absorption depends in part on C_1', it follows that the maximum absorption should be greater in those solvents which give the greater displacement of λ_1'.

In comparing with experiment we have to distinguish between mixtures with constant volumes of the two constituents and those with constant proportions by weight. To avoid further complication of formulæ, which would not affect materially the general conclusions, we ignore any change in the total volume; so that if V is the total volume, composed of volumes V_1 and V_2 of the components, we write $V = V_1+V_2$ and $P/D = p_1/d_1+p_2/d_2$.

For constant proportions by weight, $\lambda_1'-\lambda_1$ is greater as

$$p_1(1-q_1)/d_1+p_2(1-q_2)/d_2$$

is less; that is, $\lambda_1'-\lambda_1$ increases as $(1-q_2)/d_2$ decreases.

On the other hand, for constant volumes the denominator in (5) is $V_1(1-q_1)+V_2(1-q_2)$; so that $\lambda_1'-\lambda_1$ increases as $(1-q_2)$ decreases, that is, as q_2 or the refractive index n_2 increases.

4. The simplest way of testing these expressions, qualitatively at least, is to take a sample of Kundt's original experiments. For instance, 4 c.c. of an alcoholic solution of cyanine were mixed with 6 c.c. of some solvent; taking the middle of the band for methyl alcohol as zero, the displacements are shown on an arbitrary scale in Table I. There are also shown the values of $1-q_2$ and of $(1-q_2)/d_2$ for the solvents, calculated from Kundt's data.

Since constant proportions by volume were used, the order of the displacements should be that of $1-q_2$; one sees that this is practically the case, while there are considerable changes in the last column.

5. The index of extinction, $n\kappa$, has been measured by Stöckl* for solutions of iodine in various solvents. It is known that the molecular condition varies in this case; for solutions in water and alcohol, the

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* K. Stöckl, 'Messungen über Dispersion und Absorption,' Diss., Munich, 1900.

Table I.

Solvent.	Displacement.	$1-q_2$.	$(1-q_2)/d_2$.
Methyl alcohol …………	0·0	0·793	0·989
Water………………………	0·0	0·798	0·795
Acetone …………………	2·8	0·777	0·919
Alcohol …………………	3·5	0·776	0·97
Ether ……………………	4·0	0·778	1·09
Amyl alcohol……………	5·3	0·754	0·921
Ligroin …………………	5·4	0·762	1·109
Chloroform ……………	11·4	0·780	0·486
Benzol……………………	11·8	0·706	0·791
Cassia oil ………………	13·2	0·662	0·64
Carbon disulphide………	16·0	0·641	0·504

molecule is considered to be I_2, while in ether, carbon disulphide, and chloroform, it may be I_4. Taking Stöckl's results for the last three, we have

Iodine in ether …………… maximum of $n\kappa$ is $59 . 10^{-6}$ at 4770 Å.U.
„ chloroform……… „ $120 . 10^{-6}$ „ 5075 „
„ carbon disulphide „ $147 . 10^{-6}$ „ 5090 „

This agrees with the statement above, that the greater absorption is associated with the greater displacement. Also we see from Table I that the order is that of increasing refractive index. In these experiments constant weights were taken, so that the order should be that of $(1-q_2)/d_2$. This would alter the order of the last two solvents, but, on the other hand, the numerical magnitudes agree rather better, for chloroform and carbon disulphide have practically the same values, while differing considerably from ether.

6. It would be more satisfactory if dispersion formulæ were known for some absorbing substance with fair accuracy, without being too complicated. For instance, such formulæ have been elaborated for cyanine, but only by analysing the principal absorption region into seven subordinate maxima. Königsberger and Kilching* have measured the absorption and dispersion of fuchsin, and have given several estimates for dispersion formulæ; one finds that these were selected to agree with the values of $n\kappa$, but they do not give n correctly. The simplest plan is to use the following values, which agree approximately with n and $n\kappa$ in the neighbourhood of the maximum of $n\kappa$ at $5{\cdot}2 . 10^{-5}$ cm.:—

$$\frac{n^2(1-\kappa^2)}{q_1'} = 1+\frac{g\lambda^2(\lambda^2-\lambda_1'^2)}{(\lambda^2-\lambda_1'^2)^2+g'^2\lambda^2}; \qquad \frac{2n^2\kappa}{q_1'} = \frac{gg'\lambda^3}{(\lambda^2-\lambda_1'^2)^2+g'^2\lambda^2}; \qquad (6)$$

$$q_1' = 2{\cdot}15; \quad g = 0{\cdot}321; \quad g' = 8{\cdot}02 . 10^{-6}; \quad \lambda_1' = 5{\cdot}35 . 10^{-5}.$$

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* Königsberger and Kilching, 'Ann. der Phys.,' 1909, vol. 28, p. 889; also 1910, vol. 32, p. 843.

These values give a maximum of $n\kappa$ at 521 $\mu\mu$. By a calculation based on (2) and (4) we find $\lambda_1 = 4953{\cdot}8$ Å.U.

To compare with Stöckl's work we form a mixture of 0·001227 parts by weight of fuchsin with one part of alcohol, taking the densities to be 1·22 and 0·8 respectively. We have to transform the formula (6) to the form in (2) and then use the expressions in (3) and (4). We find for this solution that λ_1' is 4594 Å.U. If we take from Table I the solvent that would give the greatest change, carbon disulphide, assuming the solution to be possible, we should find $\lambda_1' = 4594{\cdot}3$ Å.U. Thus the change from alcohol to carbon disulphide would mean an inappreciable variation of 0·3 Å.U. But it must be noticed that the solutions are very dilute compared with those used by Kundt; if we made the concentration 100 times as great we should have a displacement of the order of 25 Å.U.

Using various dilute solutions of fuchsin in alcohol, Stöckl deduced from a certain type of dispersion formula the value of λ_1' in each case, and found an average value of 520·9 $\mu\mu$; he concludes that this is the position of maximum absorption for solid fuchsin. This value agrees with direct observations on the solid, but the deduction is not correct; for the undiluted absorbing substance the intensity of absorption is such that the maximum is at 10 or 15 $\mu\mu$ less than λ_1'. In addition, λ_1' for the dilute solutions should agree with the observed maxima, but these lie between 530 and 540 $\mu\mu$. One concludes that the maximum of absorption for fuchsin deduced from observations on alcoholic solutions does not agree with that observed directly in the solid substance. From the calculations above it appears that the former wave-length would be considerably greater than the latter. In this connection reference may be made to some observations which lead to a similar inference. It is known that in many solid substances, including fuchsin, rise of temperature causes a displacement of the maximum absorption towards the red; Eetschinksy* has found that a large change also occurs in the same direction when certain salts pass from the solid to the fluid state at constant temperature.

7. One must refer, in conclusion, to researches which point more directly to the formation of molecular aggregates as a chief cause of variation in absorption spectra of the same salt in various solvents, in particular to the work of Jones and Anderson and of Jones and Strong.† With solutions of certain salts of neodymium and praesodymium in mixtures of two solvents, say, water and alcohol, it is stated that two sets of bands peculiar to the two solvents co-exist in fixed positions, the intensities being functions of the

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* T. Retschinksy, 'Ann. der Phys.,' 1908, vol. 27, p. 100.

† 'Carnegie Inst., Washington, Publications,' 110 and 130, 1909—1910.

relative amounts of the solvents present. Of course, on any simple theory of Kundt's rule, such as we have given above, in using a mixture of two solvents and gradually altering the proportions, there would be a gradual displacement of the bands; one would merely add to equation (3) a term in n_3 similar to that in n_2. On this view one pictures each absorbing unit, supplied by the dissolved salt, as surrounded by the same average medium. On the other hand, the solvation theory indicates a division of the absorbers into two classes, each class composed of units with an immediate atmosphere of one of the solvents. One could only express this formally in (3) by dividing the term in λ_1 into two similar terms with slightly altered values of λ_1, but this procedure would not lead far. In the meantime, a definite expression of Kundt's rule may be of use in leading to an estimate of its effect in simple cases.

On the Resistance to the Motion of a Thread of Mercury in a Glass Tube.

By Gilbert D. West, B.Sc., East London College, University of London.

(Communicated by Prof. C. H. Lees, F.R.S. Received September 18,—
Read November 23, 1911.)

The number of physical measurements which depend on the observation of a short thread of mercury in a glass tube is considerable. Rankine's recent determinations of the viscosities of gases, by driving the gases through a tube by the pressure of such a thread, may be mentioned as an example. Notwithstanding the frequent use of the mercury thread, there does not appear to be any definite knowledge as to the connection between the motion of the thread and the forces which must act in it to produce that motion. It is the object of the present work to investigate the point.

It is comparatively well known that the upper surface of a drop of clean mercury which is slowly rising in a vertical glass tube, is more convex than when the drop is stationary, whilst the lower surface is less convex. The whole of the resistance the drop offers to motion has been attributed to this change of the angle of contact of mercury and glass. This is correct for wide bore tubes, but in narrow bore tubes viscous forces come into play.

When the drop is moving upwards with a given speed v, let α_1 and α_2 be the upper and lower angles of contact of the mercury with the glass, then the resistance to the motion due to surface tension is $2\pi a\mathrm{T}(\cos\alpha_2-\cos\alpha_1)$

where a is the radius of the tube and T the surface tension per unit length. The difference of pressure p on the two ends of the drop necessary to move the drop against the effects of surface tension is therefore

$$\frac{2\mathrm{T}}{a}(\cos\alpha_2 - \cos\alpha_1).$$

To get an expression for the effect of viscosity, it is rather more convenient to imagine the drop at rest and the walls of the tube moving downwards. The stream lines in the drop will be as shown in fig. 1, points on the surface of a cylinder of radius b within the drop being at rest.

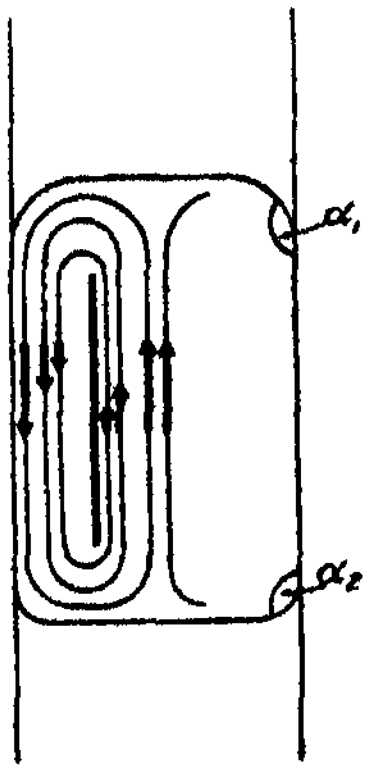

FIG. 1.

Then we have for a cylinder of radius r moving will speed $\dot{z}$.

$$2\pi r p = 2\pi l\eta \frac{d}{dr}\left(r\frac{d\dot{z}}{dr}\right),$$

where l is approximately the length of the drop, and η the viscosity of mercury.

When $r = b$, $\dot{z} = 0$, and when $r = a$, $\dot{z} = v$, the velocity of the drop, since, according to Warburg* and Villari,† there is no slip of mercury over glass. Hence

$$v = \frac{p}{4l\eta}(a^2 - b^2), \quad i.e., \quad p = \frac{4l\eta v}{a^2(1 - b^2/a^2)}.$$

Since equal quantities of liquid ascend and descend within the drop,

$$2\pi b^2 = \pi a^2, \quad i.e., \quad b^2 = \tfrac{1}{2}a^2.$$

Hence $$p = 8l\eta v/a^2.$$

The pressure P necessary to drive the drop with velocity v is therefore given by $\mathrm{P} = 2\mathrm{T}(\cos\alpha_2 - \cos\alpha_1)/a + 8l\eta v/a^2$.

Since in front of the drop mercury from the interior becomes surface mercury, and the opposite holds at the rear, there will be a temperature difference produced which adds a further resistance of the order 1 dyne. This may be neglected.

In order to test this formula, experiments were first carried out with tubes about 3 mm. in diameter. The apparatus found to be most satisfactory is represented in fig. 2.

A and B are reservoirs of compressed and rarefied air respectively, C and D are compression and suction pumps, E and F are very fine capillary tubes, G is a bromoform (density 2·9) manometer, and H is the ascent and descent tube for the thread of mercury which can be sucked up from the vessel K, after which K is lowered so as to open the lower end of H.

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* Warburg, 'Pogg. Ann.,' 1870, vol. 140, p. 367.

† Villari, 'Mem. dell' Acc. di Bologna,' 1876, (3), p. 611.

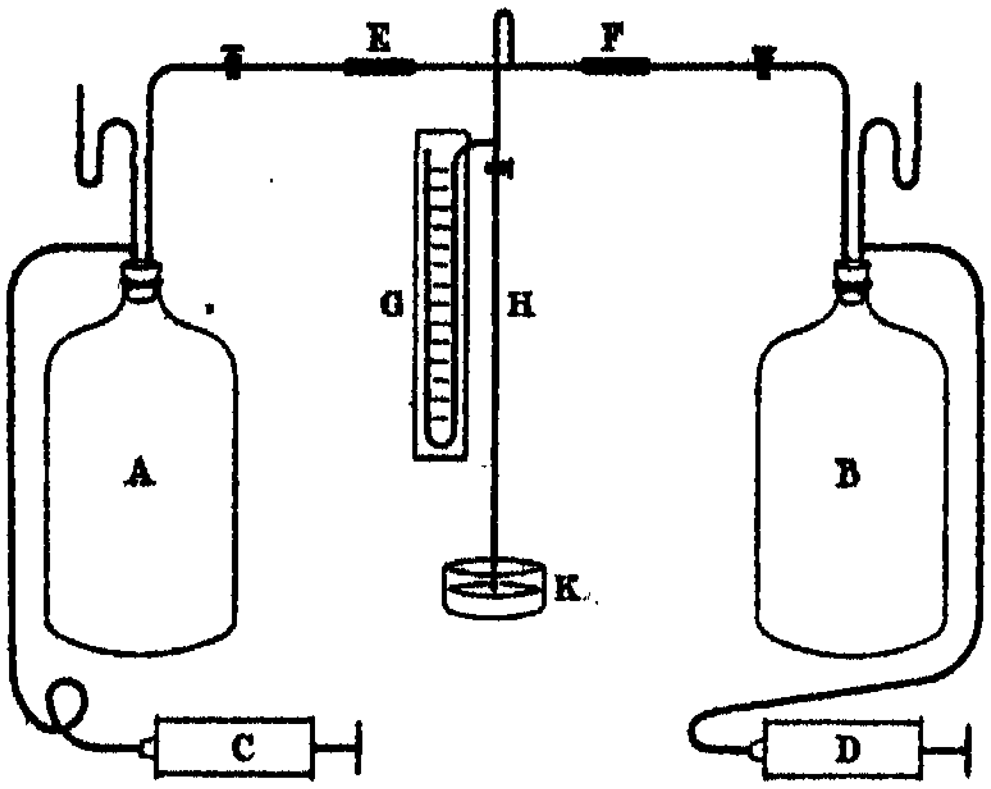

Fig. 2.

In the first apparatus the tubes E and F were absent, the drop ascended under constant pressure, and a slight constriction in the tube might stop the drop. With the capillary tube F, if a constriction occurs in the ascent tube, more air is sucked out from the space above the drop and sticking is prevented. As the pressure in the bromoform manometer varies slightly a mean of several readings is taken.

Experiments were carried out on six threads of mercury in a clean glass tube of diameter 0·264 cm. All the results obtained are exactly similar to the typical set embodied in fig. 3. A certain pressure is required to move the drop, but after that point, an inappreciable increase in pressure causes a large increase in velocity.

The results obtained with the six drops are given in brief below. The shortest thread was able to sustain itself in the tube and had to be blown down.

Length. cm.	Driving pressure for all small velocities.
6·9	0·280 cm. mercury.
4·0	0·277 ,, ,,
3·2	0·303 ,, ,,
2·5	0·294 ,, ,,
1·5	0·267 ,, ,,
0·2	0·293 ,, ,,

Within the error of experiment the driving pressure is independent of the length of the drop, and the mean driving pressure $P = 0·038/a$, when a is radius of the tube.

Hence for a tube of this diameter the term involving the viscosity of the mercury is insignificant.

Since the value of P found is not dependent on the velocity, α_1 and α_2 are not dependent on the velocity, *i.e.*, a moving drop of mercury has a front and a rear angle of contact which are independent of the velocity with which the drop is moving.

Experiments with ascent tubes of much smaller bore, to test the second term of the formula, were more difficult. Eventually a constant pressure apparatus and comparatively high velocities were used. With the smallest bore tube the times of passage over fixed lengths were obtained by means of a stop-watch, but for the others a spark photograph of the drop was taken every half-second on a film behind the tube.

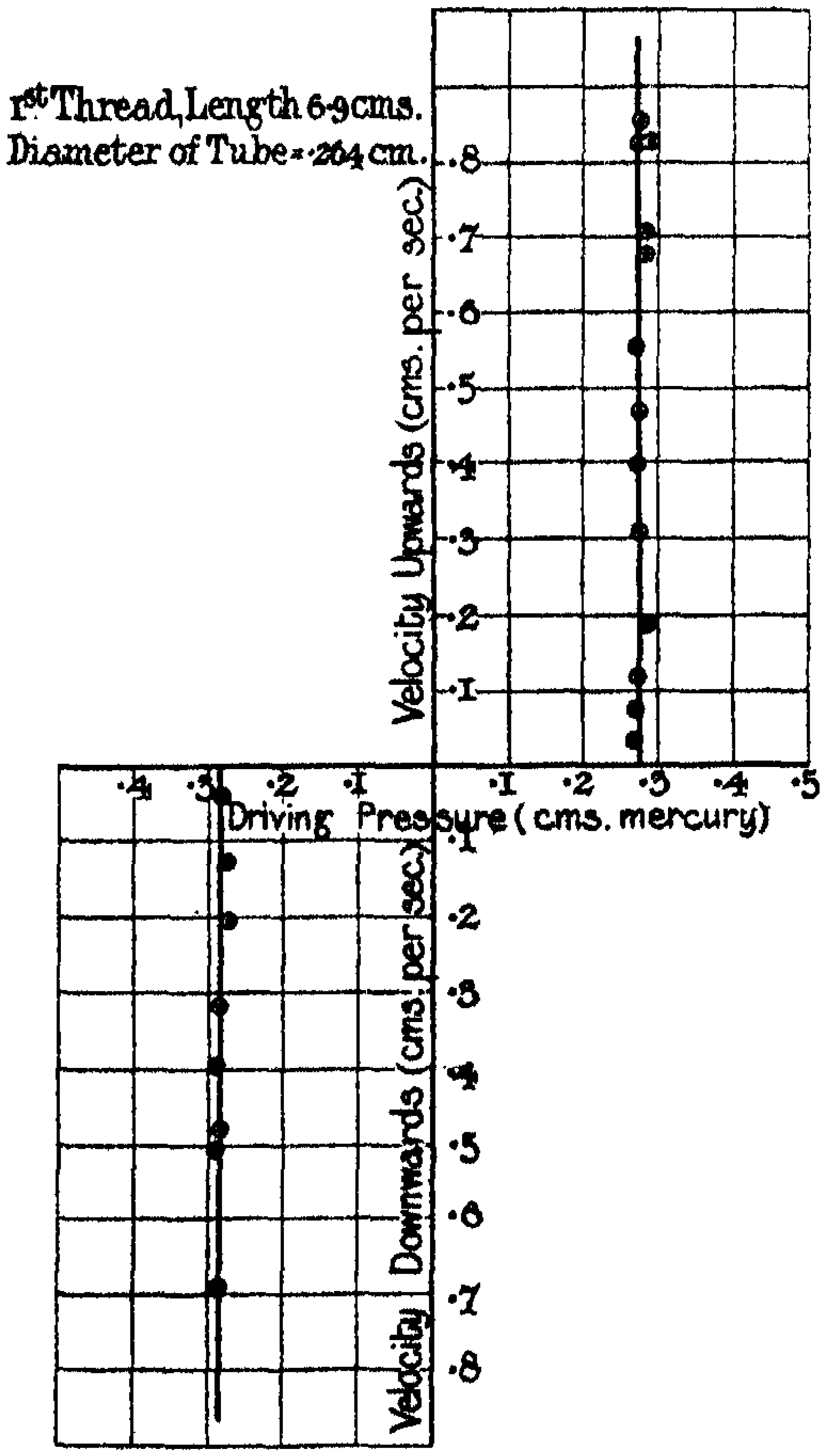

Fig. 3.

Two typical sets of results—one obtained with the stop-watch and the

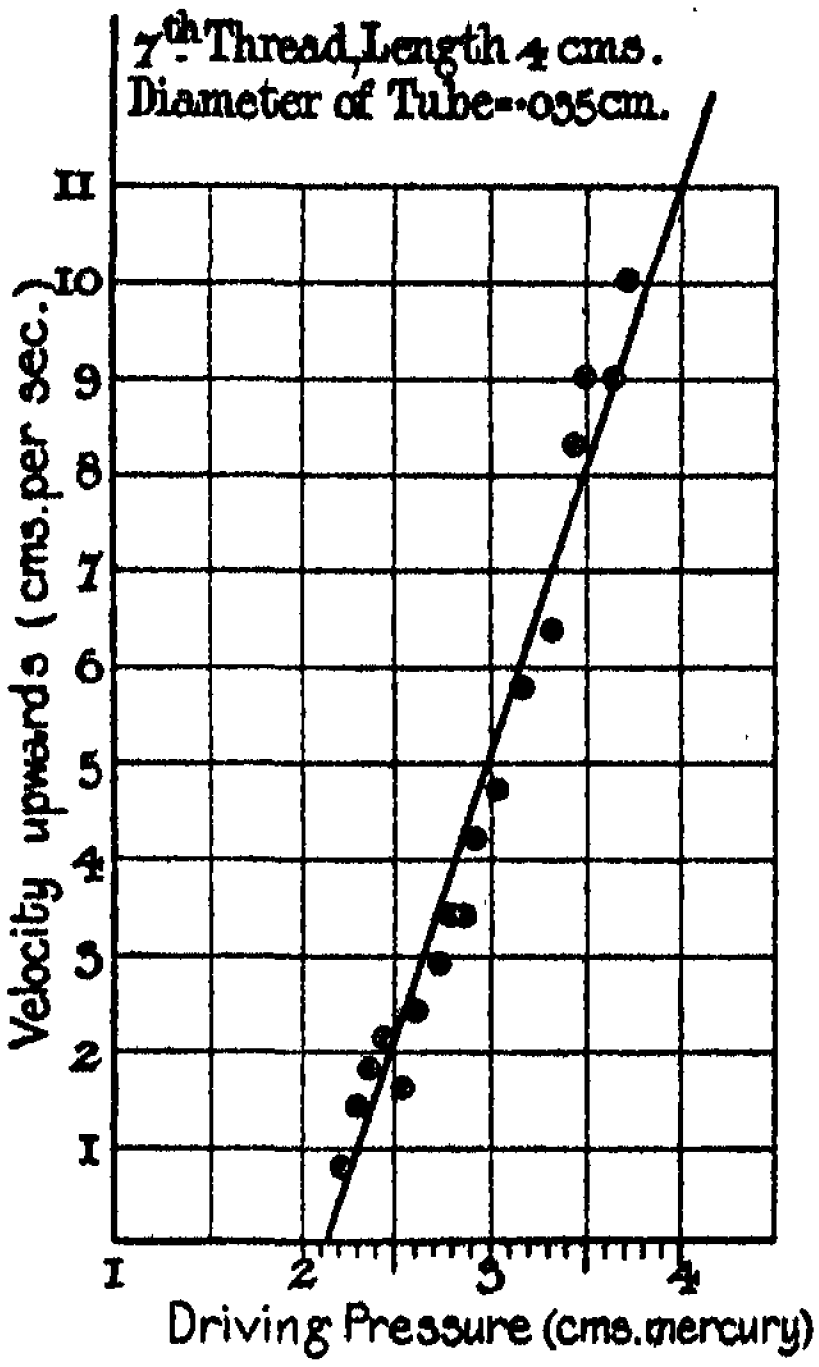

FIG. 4.

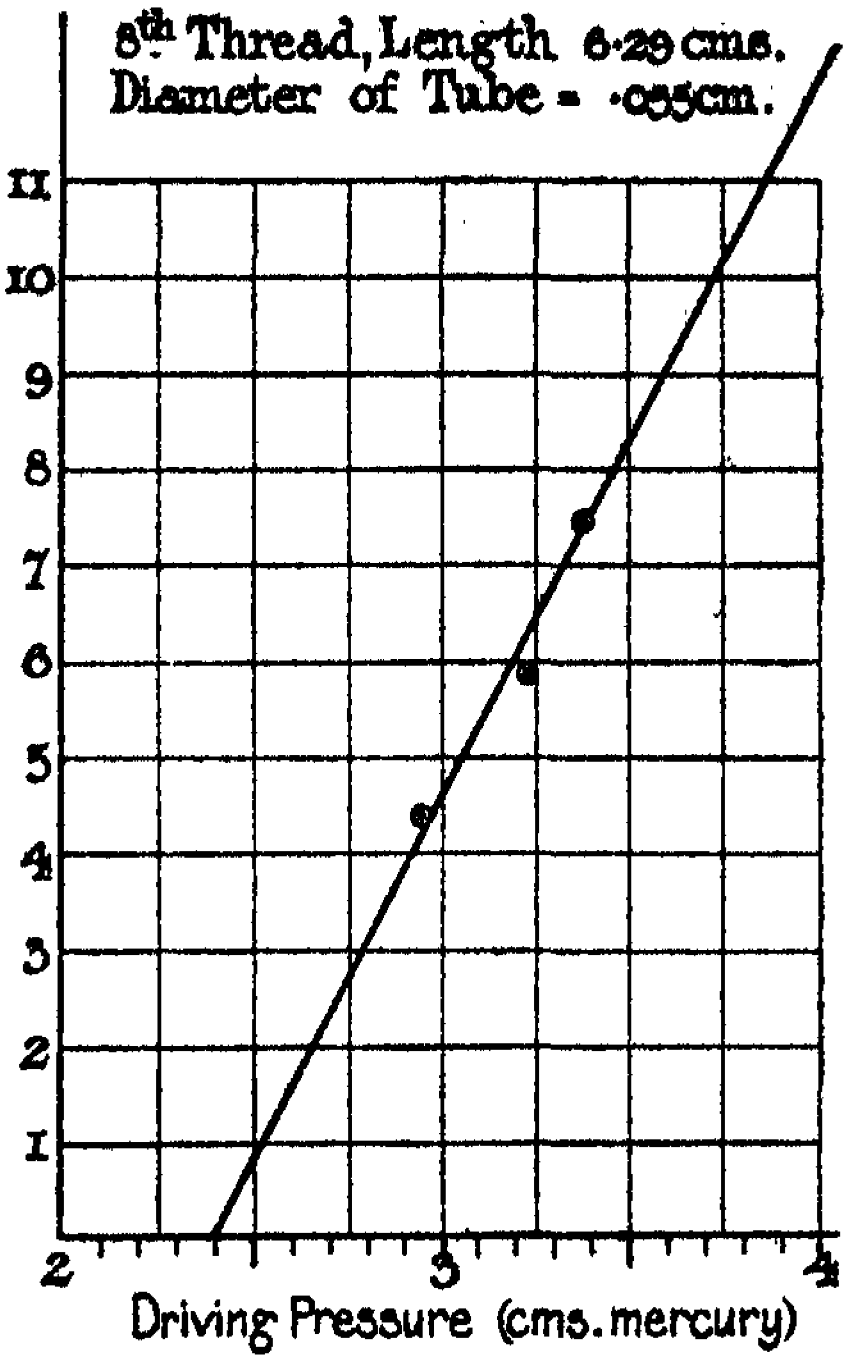

FIG. 5.

other by the photographic method—are embodied in figs. 4 and 5. The results for the finest tube are given in brief in the following table:—

Tube 0·035 cm. bore.

Length of thread.	Value of P.
cm.	
4·00	$\frac{0·0364}{a} + 0·0000127\frac{lv}{a^2}$
6·29	$\frac{0·042}{a} + 0·0000066\frac{lv}{a^2}$
3·98	$\frac{0·041}{a} + 0·0000082\frac{lv}{a^2}$
2·29	$\frac{0·039}{a} + 0·0000180\frac{lv}{a^2}$

$$\text{Mean P} = \frac{0·039}{a} + 0·00001\frac{lv}{a^2}.$$

The mean value of the first term obtained from experiments on wide tubes $= 0·038/a$.

The theoretical value for the last term (taking η at 19° C., the mean temperature of the experiments, = 0·016) is 0·0000093 lv/a^2. The agreement is sufficiently close.

It is therefore clear that the velocity v of a thread of mercury l cm. long, in a glass tube of uniform radius a, subject to a driving pressure P, is represented, with a fair degree of accuracy, by the equation

$$P = \frac{0 \cdot 038}{a} + \frac{8l\eta v}{a^2}.$$

In conclusion I should like to acknowledge my indebtedness to Prof. Lees for much valuable assistance, and to the Research Committee of the East London College for the apparatus.

The Adherence of Flat Surfaces.

By H. M. Budgett, B.A.

(Communicated by R. T. Glazebrook, C.B., F.R.S. Received September 20,—
Read November 23, 1911.)

In recent years it has been found possible to polish plane surfaces of hardened steel to a degree of accuracy which had previously been approached only in the finest optical work, and to produce steel blocks in the form of end gauges which can be made to adhere or "wring" together in combinations. Considerable interest has been aroused by the fact that these blocks will often cling together with such tenacity that a far greater force must be employed to separate them than would be required if the adhesion were solely due to atmospheric pressure. It is proposed in this paper to examine the various causes which produce this adhesion: firstly, showing that by far the greater portion of the effect is due to the presence of a liquid film between the faces of the steel; and, secondly, endeavouring to account for the force which can be resisted by such a film.

The only previous experiments in this direction appear to be those carried out with Whitworth surface plates by Prof. Tyndall in 1875.* By wringing together two of these plates and suspending them in a vacuum he proved that the adherence between them was not caused solely by atmospheric pressure as had been previously supposed. According to Goodeve,† the conclusion at which Tyndall arrived was that the plates adhered by the molecular attraction of the bearing points brought into close contact by reason of the near approach to absolute truth of surface. Frequent references have been made to these experiments, and the conclusions of Tyndall appear to have been generally accepted.

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* Paper read at the Royal Institution by Prof. Tyndall, June 4, 1875.

† 'The Elements of Mechanism,' 1897, pp. 272—273.

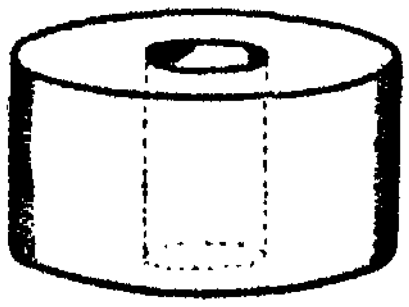
The author's curiosity was aroused by the fact that some steel gauges which he was constantly using in combinations did not always cling together with the same force. Frequently they refused to adhere to one another at all, whilst at other times considerable difficulty was experienced in getting them apart. On one occasion, when two blocks had been left wrung together for a long time, it was found necessary to hold one in a vice and hit the other sharply with a hammer in order to separate them. Subsequent examination showed that the faces had rusted together, which proved that some moisture must originally have been present between them. This led to the discovery that a minute film of condensed water vapour always formed upon the steel when the blocks were held with warm hands, and if care were taken to avoid this, and the faces were thoroughly cleaned with alcohol to remove grease, then all signs of adhesion vanished, and the blocks would fall apart at once under their own weight. It soon became clear that the wringing effect was chiefly due to the presence of a liquid film between the blocks, and it was decided to make a series of experiments in order to examine—

(1) The adhesive properties of various liquid films.

(2) The effects of atmospheric pressure.

(3) The force of attraction between the molecules of steel in the two surfaces.

For these experiments a number of hardened steel blocks were specially made in the form of cylinders 1 inch in diameter and ½ inch deep, having a central screwed hole 5/16 inch in diameter, the area of the faces being thus 0·7 square inch. These were specially polished with great care so that their faces were true planes within one-millionth of an inch, the accuracy being optically tested by means of proof glasses.



In testing the adhesive properties of various liquid films the following procedure was adopted:—The liquid under examination (with the exception of condensed water vapour) was applied with a piece of clean linen to the faces of two blocks which had previously been thoroughly washed with alcohol and allowed to regain their normal temperature. The superfluous liquid was wiped off until only the barest film remained, until, in fact, the ordinary observer would say that the faces were perfectly dry. In the case of condensed water vapour the blocks were held for an instant in the hands, or near the breath, to allow a film of moisture to spread over the steel, and were then quickly put together before evaporation could take place. The blocks were next wrung together with a combined sliding and twisting motion, which was found to produce maximum results, and after a pair of screwed handles had been attached the force required to separate them normally was noted on a spring balance. Many hundreds of readings were taken with dozens of pairs of blocks, and the average and maximum results are given in Table I, whilst some typical readings actually obtained with one pair of blocks are given in Table II.

Table I.

(Results obtained with many pairs of blocks.)

Liquid.	Pull in lbs. at separation.	
	Average.	*Maximum.*
Condensed water vapour	35	65
Turpentine	29	89
Paraffin	27	46
Oil of almonds	24	85
Lubricating oil (Price's)	22	80
Olive oil	20	83
Sperm oil	18	30
Rangoon oil (Price's)	17	28

Table II.

(Typical results actually obtained with one pair of blocks.)

Liquid.	Pull in lbs. at separation.	Average.
Condensed water vapour	38, 82, 41, 41, 38, 85, 48, 88, 28, 42, 31, 45	87
Turpentine	25, 81, 24, 27, 28, 80, 80, 24, 29, 31, 28, 81	28
Paraffin	29, 25, 22, 22, 80, 23, 28, 25, 29, 22, 27, 27	25
Oil of almonds	22, 22, 22, 25, 18, 25, 25, 28, 21, 21, 25, 23	23
Lubricating oil (Price's)	20, 22, 28, 24, 20, 18, 25, 28, 25, 24, 26, 25	23
Olive oil	19, 21, 17, 16, 15, 20, 16, 18, 21, 16, 16, 18	18
Sperm oil	23, 20, 19, 20, 16, 15, 19, 17, 22, 20, 17, 16	19
Rangoon oil (Price's)	12, 17, 19, 15, 22, 18, 13, 21, 20, 17, 15, 14	17

Considerable variation in the readings is unavoidable, as it is impossible to gauge exactly the thickness and uniformity of the applied films, and there is an element of uncertainty in the action of sliding the blocks together. Minute particles of dust and fluff off the linen have to be avoided with great care, and after a time the extreme accuracy of the faces becomes impaired, owing to the strain and to scratches which cannot be altogether prevented. To obtain the most uniform results it was found desirable to allow the blocks to stand for some time after each reading, in order that their temperature might remain as constant as possible.

No adhesion could be obtained with volatile liquids, such as alcohol, benzine, and petrol; and viscous liquids, such as glycerine, treacle, and glucose, produce very little effect. By rubbing the blocks on the hands after they have quite recently been washed very great adhesion takes place, and readings as high as 90 lbs. were recorded. This must be due to traces of soap remaining on the hands, as only ordinary adhesion is obtained if all soap is carefully removed by rinsing the hands in clean water. Several attempts were made to apply soap films by other means, but these were unsuccessful.

In order to determine what were the effects of atmospheric pressure, arrangements were made by which, after being wrung together, the blocks could be separated in a vacuum. This was accomplished by means of a rod passing through an air-tight gland in the glass bell jar of a vacuum pump, and fixed to a spring balance within the jar. The lower end of the spring balance could be screwed through a universal joint into the upper block under test, the lower block being screwed to the plate of the pump. The blocks were separated alternately in air and *in vacuo*, and the average results compared as shown in Table III.

Table III.

(Comparing Load at Separation in Air and under Vacuum.)

Liquid.	Average of 12 readings in air.	Average of 12 readings in vacuo.	Difference.
			lbs.
Condensed water vapour ...	36·1	34·2	1·9
Turpentine	31·7	30	1·7
Paraffin	25·7	24·6	1·1
Oil of almonds	25·1	22·1	3
Lubricating oil (Price's) ...	22·6	19·1	3·5
Olive oil	19	15·7	3·3
Sperm oil.......................	18·7	14·3	4·4
Rangoon oil (Price's).........	15·9	12	3·9

So little difference was found between the two sets of readings that it was decided to check the results by the following method:—The load was increased by small steps, whilst the air was alternately exhausted from and admitted to the bell jar. If separation occurred when air was present the *maximum* pull due to atmospheric pressure was obtained by comparison with the preceding reading *in vacuo*. If, on the other hand, separation took place *in vacuo*, a comparison with the last reading in air gave the *minimum* pull due to atmospheric pressure. The results so obtained are given in Table IV, and are found to confirm those in Table III.

Table IV.

(Comparing Load at Separation in Air and under Vacuum.)

Liquid.	No separation in air.	Separation in vacuo.	Separation in air.	No separation in vacuo.	Lower limit of effect of atmospheric pressure.	Upper limit of effect of atmospheric pressure.
					lbs.	lbs.
Condensed water vapour	36	35·5	37	35	0·5	2
Turpentine	30	29	31	28·5	1	2·5
Paraffin	28	27·5	27	25	0·5	2
Oil of almonds	20	17·5	24	20	2·5	4
Lubricating oil	22	19	21	16	3	5
Olive oil	20	17·5	22	17·5	2·5	4·5
Sperm oil..................	19	16	19	14	3	5
Rangoon oil..............	15	12	17·5	12·5	3	5

It is surprising to note that the force due to atmospheric pressure in no case exceeds 5 lbs., as, the area of the faces being 0·7 square inch, it might have been expected that this force would have approached 10·5 lbs. One would naturally suppose that such accurate surfaces, with a grease film between them, would be perfectly air-tight. It is evident, however, that air must have free access to a very large area of the faces, probably owing to the blocks being pulled apart or distorted slightly under the strain of the applied force, the film between them stretching before breakage occurs. It must be remembered that the volume required to fill the space between the faces is exceedingly minute, and since the pull is increased very gradually, a considerable time is allowed for the air to leak in or out. With thicker films the atmospheric pressure has a greater effect. Thus, with a fairly thick layer of Rangoon oil a difference of 6·5 lbs. was noted between the force of separation in air and *in vacuo*, the force due to the air in this case being 9·3 lbs. per square inch. This may be due to the air being more impeded by the thick oil, or to the faces being less distorted or separated, owing to a smaller force being required to cause breakage when a thick film is present. On the other hand, when the faces are perfectly clean and no film whatever is present, the adhesion almost vanishes and the blocks will not support each other, although their weight is only 1¼ ozs., showing that in this case the force due to atmospheric pressure is almost eliminated. For the same reason it is obvious that the force due to the attraction of the molecules of steel in the opposing faces is quite negligible in comparison with those which we are considering, and it is not proposed to describe here the experiments which were made in this direction, although it is possible that these may be dealt with in a separate paper.

It seems probable that the results obtained by Tyndall in his experiments must be attributed to the presence of traces of grease or moisture on the surfaces of the plates rather than to molecular attraction, and we must conclude from our examination—

(1) That at least 75 per cent. of the adhesion is caused by the presence of a liquid film between the faces in contact.

(2) That not more than 25 per cent. is due to atmospheric pressure.

(3) That the adhesion practically vanishes when no film is present.

(4) That the attraction of the molecules of steel in one face by the molecules of steel in the opposite face is negligible.

If we assume that the film is continuous and covers the whole area of the steel, then, since the distance between the blocks is very small, it is known that

$$F = 2AT/d,$$

where F is the force drawing the blocks together, T is the surface tension of the liquid, A is the area of the faces, and d is the distance between them. In the case of a paraffin film, F is 46 lbs. (from Table I), T is 31 dynes per centimetre, or about 0·00017 lbs. per inch, A is 0·7 square inch. Substituting these values, we find that the theoretical distance between the blocks is approximately 0·000005 inch. Their distance apart must actually be less than this, as, even when several blocks are wrung together, no increase in their total length, as compared with the sum of their separate lengths, can be detected on an extremely sensitive measuring machine.

Microscopic examination, however, shows that the applied films are far from being continuous membranes. Fig. 1 is a micro-photograph showing the distribution of a paraffin film before the blocks have been put together. It will be seen that the liquid is collected into small drops, which are still left adhering to the steel after the faces have been wiped. Attempts were made to obtain a more uniform distribution of the liquid by a method mentioned by Lord Rayleigh in his recent article on "Breath Figures."* The point of a blowpipe flame was rapidly passed over the clean faces of the blocks, in the hope that after cooling a more even film of condensed water vapour would be obtainable. It was found, however, that oxydisation took place and the faces were impaired. No improvement in the film distribution was noticeable after the blocks had been washed in strong caustic potash, or momentarily dipped in dilute nitric acid.

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* 'Nature,' May 25, 1911.

It is, of course, impossible to photograph the film when the blocks are together, but, by going through the process of wringing and then *sliding* the blocks apart, it is possible to gain a fair idea of the effect of wringing upon the distribution of the film. Fig. 2, which was obtained in this way with the paraffin film, shows that the small drops have been drawn out and distributed in thin lines, which are approximately equally spaced and parallel. These lines are spread over the whole of the faces of the blocks, and their uniformity is very remarkable. The approximate total length of these lines was ascertained in order to determine what pull would be necessary to overcome surface tension across a section of the liquid midway between the faces of the blocks; the edges of the liquid being normal to

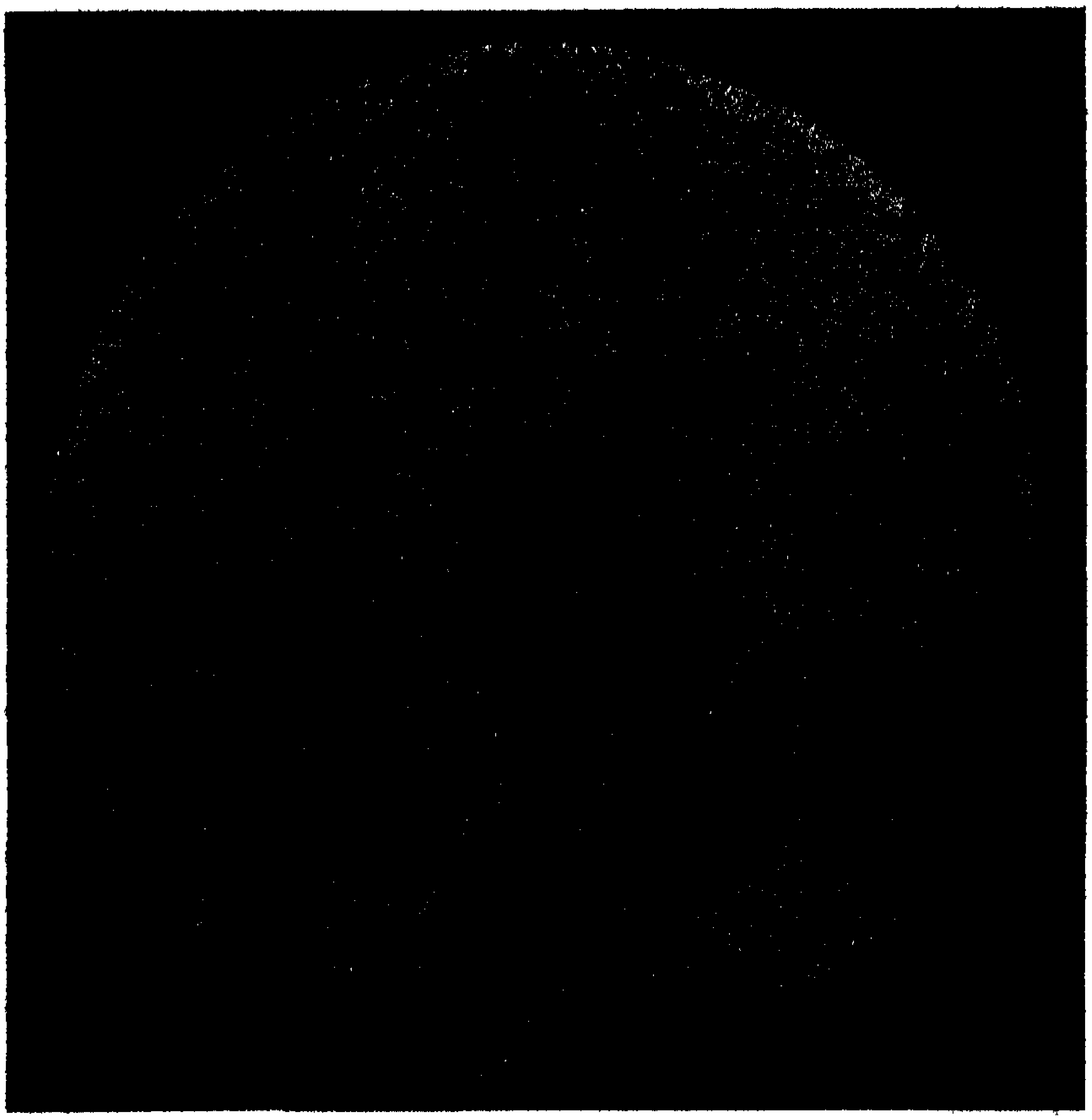


Fig. 1.—(× 206 diams.).

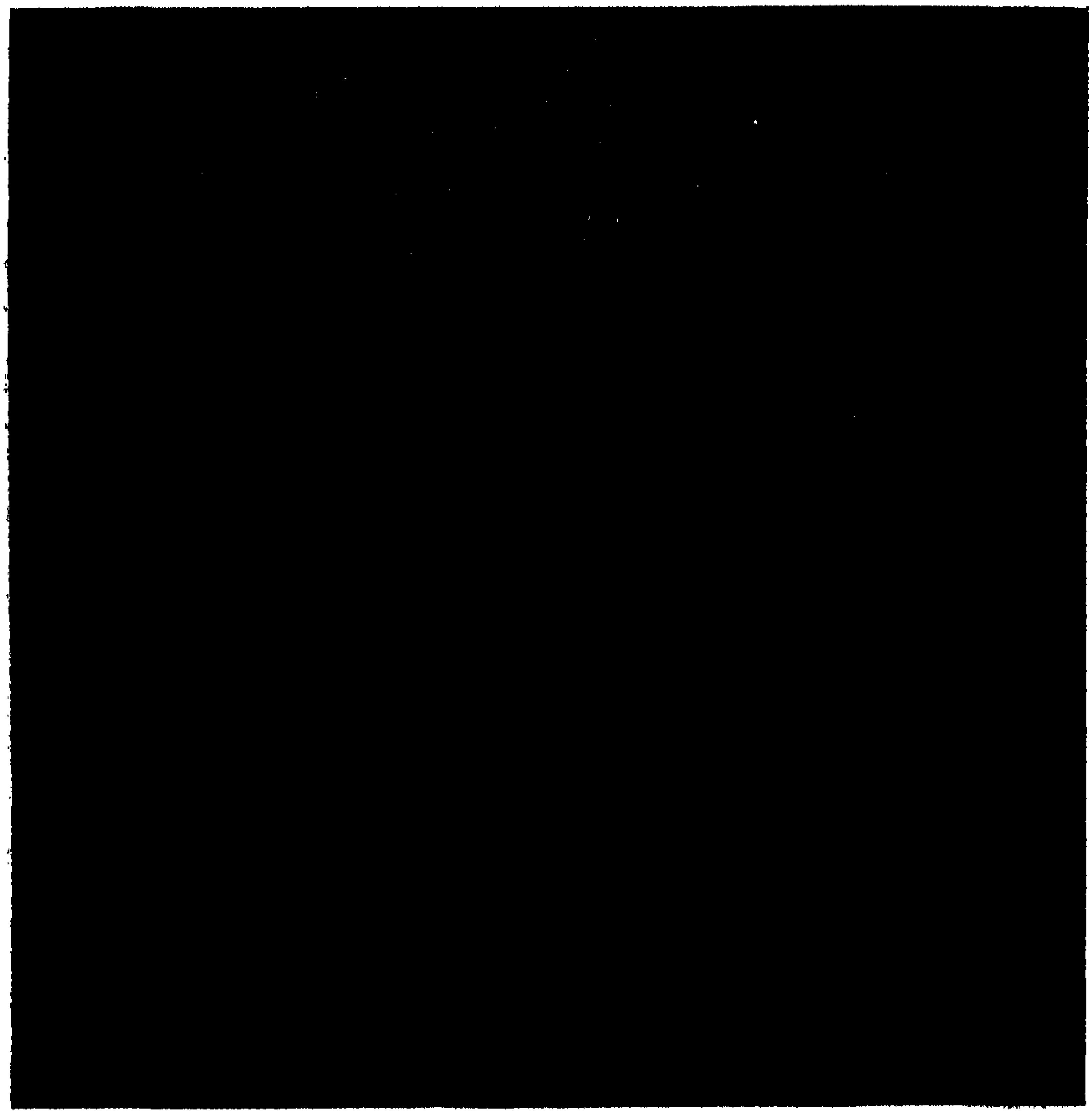
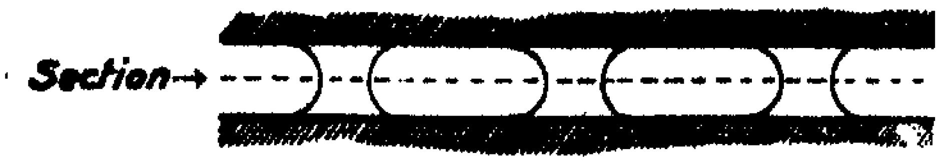


Fig. 2.—(× 176 diams.).

the faces at all points on this section. The distance between the lines was measured by means of a micrometer eyepiece, and by taking a number of



readings at various points on the surface, it was found that there were on the average about 170 lines per millimetre. Since these lines completely cover the faces of the blocks it is easy to calculate their total length. The area of the faces is 0·7 sq. in. or 450 sq. mm., and the length per square millimetre is 170 mm., so that the total length is approximately 7650 cm. In calculating the surface tension we have to take each side of the lines into consideration, so that

$$L = 2 \times 7650 = 15{,}300 \text{ cm.}$$

Also T is 31 dynes per centimetre for paraffin.

Hence, if P is the pull required to overcome surface tension at this section, we have, $P = TL = 31 \times 15,300 = 474,300$ dynes, or, slightly over 1 lb. We must, therefore, conclude that only a very small proportion of the force necessary to rupture the film (assuming it to break in the centre) is due to the ordinary phenomena of surface tension, and consequently that the molecular cohesion of the liquid must bear practically the whole of the strain across this section.

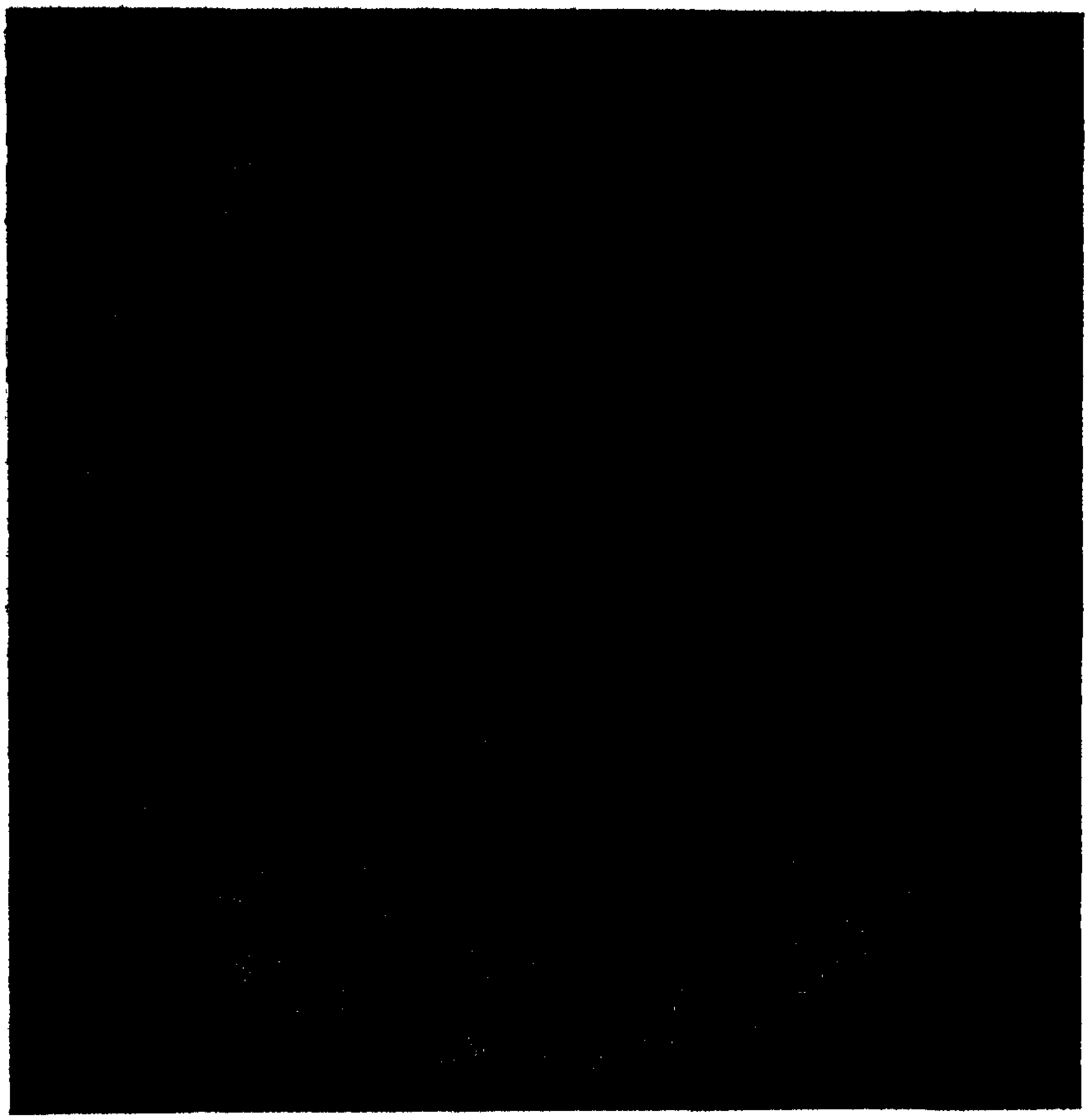


FIG. 3.—(× 234 diams.).

Fig. 3 is a micro-photograph showing the distribution of the paraffin after the blocks have been pulled apart, and at first sight it is not easy to say whether the film has broken in the middle, leaving one half on each block, or whether the liquid has parted from the steel. The former appears to be the case, as it is unlikely that the distribution would be so uniform if the liquid were torn away from the metal, in which case one would expect to find patches free from moisture on one of the blocks. As the liquid always appears to be distributed very equally between each of the blocks after breakage has occurred, even when one of them has been left perfectly dry before wringing, it is probable that rupture takes place in the liquid itself.

In 1877 it was shown by Prof. Osborne Reynolds* that liquids, from which air bubbles have been carefully expelled, can withstand a considerable pull without rupture. Prof. Worthington,† employing a method discovered by Berthelot,‡ of allowing a liquid to cool in a sealed glass tube which it completely filled when warm, obtained a tension of over 17 atmospheres with alcohol before breakage, whilst by the same method Messrs. Dixon and Joly§ recorded a tension of 7 atmospheres for water.

Amongst these experimenters there is a consensus of opinion that the liquid parts from the tube (possibly owing to a bubble forming more easily on the glass) so that the ultimate breaking strain of the liquid itself is not determined in this manner.

Referring to fig. 2, we see that before breakage the film certainly does not cover more than one-half of the area of the faces; when the pull is applied and the liquid is drawn out the area must become much less. This is borne out by fig. 3, showing how the paraffin is collected together into little drops, quite separated, and covering not more than one-tenth of the area of the steel. It is probable that just before breakage occurs the cross section is still further reduced, but for purposes of calculation we will take it that the area of paraffin under strain is one-tenth of the area of the faces of the blocks, *i.e.*, 0·07 square inch. Films of condensed water vapour and turpentine evaporate too quickly to allow of microscopic examination; but assuming that the cross section of the liquid in these cases is the same, viz., 0·07 square inch, and making the necessary deductions for atmospheric pressure and surface tension from the values given in Table I, we obtain the following results:—

Liquid.	Average breaking strain.	Maximum breaking strain.
	lbs. per sq. in.	lbs. per sq. in.
Condensed water vapour......	443	871
Turpentine	371	514
Paraffin	343	614

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* 'Memoirs of the Manchester Lit. and Phil. Society,' session 1877–78.

† 'Phil. Trans.,' A, 1892, p. 355.

‡ 'Ann. de Chimie,' 1850, vol. 30, pp. 232—237.

§ 'Phil. Trans.,' B, 1895, p. 568.

These figures for the ultimate breaking strain of liquids are far higher than those previously obtained by other methods, probably owing to the fact that no air bubbles of any magnitude can possibly be present in the films, and the action of wringing the blocks together must bring the liquid into very intimate contact with the steel. It does not appear to be likely that results of this magnitude could ever be obtained with larger volumes of the liquids, and, in fact, if the thickness of the film is increased the pull required to cause separation rapidly diminishes. Thus if the blocks, when cold, are held by a person having very warm, damp hands, an excess of moisture is deposited upon the steel, and it is difficult to obtain any wringing effect until the blocks have warmed up and some of the liquid has evaporated.

It appears that there is a limit to which the thickness of the film can be reduced, and when this is reached the liquid will seize to the steel. The sliding and twisting of the blocks tend to further reduce the thickness by spreading the liquid, and this action is strongly resisted by the film, considerable force being necessary to move the blocks over one another. Soft metals will not stand the strains put upon them in this manner by the films between them, and pieces may actually be dragged out of their polished surfaces. This is also very noticeable in glass, and it is essential that optical proof planes should be perfectly free from grease before use, as otherwise they will be ruined. During the manufacture of lenses and proof glasses the faces are always cleaned with spirit or benzine before being put together, but this precaution appears to be taken more as a matter of traditional routine than owing to the knowledge of why it is necessary.

As a result of our examination, we are led to the following conclusions:—

1. Breakage occurs in the liquid itself, and not between the liquid and the steel.
2. Only 4 per cent. of the force required to rupture the film is due to surface tension.
3. The remaining 96 per cent. must be necessary to overcome the molecular cohesion of the liquid.
4. The tensile strength of water may, under special conditions, amount to nearly 60 atmospheres.

The author's thanks are due to Mr. E. Senior for the care which he has taken in the difficult task of preparing the micro-photographs to illustrate this paper.

On the Spectrum of Boron.

By Sir WILLIAM CROOKES, O.M., For. Sec. R.S.

(Received September 25,—Read November 9, 1911.)

[PLATE 1.]

The first published account I can find of the ultra-violet spectrum of boron is by W. N. Hartley in 1883,* who obtained it by submitting saturated solutions of boric acid and of borax to the action of an induction spark. He describes it as consisting of three strong lines, of wave-lengths 3450·3, 2497·0, and 2496·2.

Rowland, in his "New Table of Standard Wave-lengths,"† gives the wave-lengths of two boron lines as 2497·821 and 2496·867. He does not mention a third line.

In 1893 J. M. Eder and E. Valenta‡ gave a list of 17 lines in the ultra-violet spectrum of boron, their wave-lengths being:—

3957·0
3941·7
3829·3
3824·5
3451·3*
3246·9
2689·0
2688·2
2497·7*
2496·8*
2388·5
2267·0
2266·4
2088·8
2088·4
2066·2
2064·6

* The lines so marked are the dominant lines.

In 1897 F. Exner and E. Haschek§ recorded eight lines in the ultra-violet spectrum of boron, their wave-lengths being:—

3451·4*
3246·7
2688·2
2687·3
2497·8*
2496·88*
2267·03
2266·47

* The lines so marked are the dominant lines.

In 1902 Exner and Haschek again took measurements of the lines in the ultra-violet spectrum of boron from a sample of boric acid obtained from Merck, and gave the wave-lengths of the three lines as 3451·49, 2497·79, and 2496·87.

In 1904 A. Hagenbach and H. Konen‖ published photographs of the boron spectrum in which the wave-lengths of the dominant lines are given as

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* 'Roy. Soc. Proc.,' vol. 35, p. 301; and 'Chemical News,' vol. 48, p. 1.

† 'Phil. Mag.,' 1893, vol. 36, p. 49.

‡ 'Akad. der Wissensch. in Wien,' Denkschriften, vol. 60.

§ 'Akad. der Wissensch. in Wien,' July, 1897, vol. 106.

‖ 1905, Jena, G. Fischer; London, W. Wesley.

3451, 2498, and 2497. The spark was taken between carbon poles with boric acid. Many other lines are shown, but the authors ascribe these to the electrodes.

In March, 1901, I was examining the silicon spectrum, using fused silicon electrodes, and a pair of lines were seen at about 2497 and 2498 which could not be found in any silicon spectrum photographed by other observers. I soon identified these strangers as lines given by a boron impurity in the fused silicon. A pure sample of fused silicon supplied by Johnson and Matthey did not show these lines.

Properties of Boron.

Amorphous boron when pure is a fine dark brown powder. Its conductivity for electricity is very poor, and it is difficult to manipulate so as to get an induction spark through, as it is readily blown away. I could not fuse it in the arc.

Quite recently Dr. Weintraub, of the West Lynn Research Laboratory, General Electric Co., U.S.A., has prepared boron in a solid state and chemically pure. Hitherto the physical properties of this element were unknown, notwithstanding the efforts of many chemists who had worked on the subject. Moissan, who came nearest to obtaining the pure element, only succeeded in getting it in the form of an amorphous powder. He said it was not possible to melt or volatilize boron in a carbon crucible or arc as it was changed into carbon boride, and concluded that boron passed from the solid to the gaseous state without becoming liquid.

Dr. Weintraub has not only obtained boron in a state of purity, but has prepared it in a fused homogeneous form. His process consists in running one or more alternating current arcs, fed by a high potential transformer, between water-cooled or air-cooled copper electrodes, in a mixture of boron chloride with a large excess of hydrogen in a glass or copper vessel. The boron is thrown off in fine powder on to the walls of the vessel, or agglomerates on the ends of the electrodes, where it grows in form of small rods. After a while the arc runs between two boron electrodes, and if the current is of proper value the rods melt down to boron beads which eventually fall off, whereupon the same process repeats itself.

The first specimens I received from Dr. Weintraub were deposited from a vaporous state from boron chloride and hydrogen in the manner already described. Subsequently I received some lumps of fused boron which had been prepared from magnesium boride obtained in the reaction between boric anhydride and excess of magnesium. The magnesium boride dissociates at a relatively low temperature (1200°), especially *in vacuo*, and with rapidity at 1500°. The fusion is effected between copper electrodes. Under the conditions of the experiment no disintegration takes place, and according to my informant, the affinity of copper for boron is so slight that it can be directly fused on to the electrode without being contaminated with copper. Another way of fusing boron is in what Dr. Weintraub terms a mercury arc furnace, based on the fact that most refractory bodies, such as tungsten, tantalum, boron, etc., have no affinity whatever for mercury.

The fused lumps of boron obtained by the reaction between boron chloride and hydrogen were found by Dr. Weintraub to be quite pure, analysing from 99·8 to 100·2 per cent., the difference being due to errors of experiment, and perhaps to a trace of silica abraded from the agate mortar during pulverisation.

The boron prepared by fusing that obtained by the gas process is not quite so pure. The sample sent me contains about 97 per cent. boron, the main impurities being nitrogen in the form of boron nitride, magnesium in the form of magnesium boride, a trace of iron, and a trace of carbon.

The most interesting property of solid boron is its extraordinary rise in electric conductivity with slight increase in temperature. A piece of fused boron measured by Dr. Weintraub, which at the room temperature (27° C.) had a resistance of 5,620,000 ohms, dropped to 5 ohms at a dull red heat.

Another noteworthy property of both the melted and agglomerated boron is extreme hardness. It comes next to the diamond in hardness, a splinter easily scratching corundum. Its fracture is conchoidal, and when melted no decided crystalline structure is seen. The agglomerated boron, deposited in the arc from boron chloride and hydrogen, is, on the contrary, highly crystalline. A rod of boron heated to whiteness before the blowpipe shows no sign of fusion, but the flame is coloured green, and when the cold rod is microscopically examined it is seen to be covered with minute globules of fused boric anhydride.

The first samples of boron under experiment were of the agglomerated variety, in the form of thin flakes deposited from the vaporous condition in the reaction already described. Several fragments were clamped together to form the electrodes.

It is not easy to get the spark to pass between cold boron poles owing to its high electrical resistance. When the two pole pieces are held in brass clips in front of the spectroscope, the spark passes across from one clip to another; it is only when the boron poles get heated by the spark that they begin to conduct sufficiently to let the current pass. The light of the spark is somewhat feeble, and exposures from 1 to 2 hours are required to bring out with intensity the three dominant lines. Generally, when the boron electrodes are well heated the current assumes the form of a minute arc, starting from a luminous point at one edge of the pole, which soon becomes red-hot. Occasionally an intense yellow-green flame shoots from a corner, which immediately fuses, but this only lasts a few seconds. After the current has passed for 40 or 50 minutes an accumulation of boric anhydride causes a resistance to the current, and it then again begins to pass across between the brass clips.

The melted boron is easier to manipulate in the spectrograph. In the form of solid blocks the electrodes do not get so hot, and very little oxidation takes place. The spark is of a faint apple-green colour, and when the poles have become sufficiently hot to carry the current it passes quietly for hours without change.

The spectrum of boron consists essentially of three lines, the wave-lengths of which, according to careful measurements made in the manner described in 1903, are 3451·50, 2497·83, and 2496·89.* For easy comparison I give in a tabular form the wave-lengths of these lines measured by different observers:—

Hartley (1883)	3450·3	2497	2496·2
Rowland (1893)	—	2497·821	2496·867
Eder and Valenta (1893)	3451·3	2497·7	2496·8
Exner and Haschek (1897)	3451·4	2497·8	2496·88
„ „ (1902)	3451·49	2497·79	2496·87
Hagenbach and Konen (1908)	3451	2498	2497
Crookes (1911)	3451·50	2497·83	2496·89

Besides these three lines two others of wave-lengths about 3274 and 3248 were seen on the photographs of each sample of boron, the agglomerated and the melted, the lines in the melted being the stronger. The fact that no other observer had noticed these lines, and their being of different intensities in the two samples, proved that they were due to some other element accidentally present. A run over my photographed spectra of the elements soon showed these lines to be the dominant copper lines, 3274·096 and 3247·688. A short time ago Sir Walter Noel Hartley† traced the occurrence of these two copper lines in the spectrum from pure cadmium electrodes to the proximity of his laboratory to the overhead conductors of the tram-lines. The condensation of the vapour of copper following the sparking at the rubbing contact yielded a dust of extreme tenuity, such as could not arise from mechanical abrasion of the solid metal. Sir Walter Noel Hartley found that the amount of copper passing between the sparking terminals sufficient to produce an impression of the copper lines on the photographic plate need not be more than from 0·001 to 0·0014 mgrm. This explanation could not apply to my own case, for no tram-lines are near the laboratory, and nothing was going on that could give rise to a dust of copper. The atmosphere of my laboratory was perfectly free from any trace of copper, but the clips that hold the electrodes in front of the slit of the spectrograph were made of brass. When the spark first passes the boron is cold, and in that condition is a very bad conductor; consequently, some discharge may take place between the brass clips. After a little time, however, the boron gets hot enough to conduct the whole current.

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* "The Ultra-Violet Spectrum of Radium," 'Roy. Soc. Proc.,' 1903, vol. 72, p. 295.

† 'Roy. Soc. Proc.,' vol. 85, p. 271.

To guard against such an accidental contamination, I made a pair of clips of pure gold for boron and other electrodes, and repeated the spectrographic tests with each sample of boron.

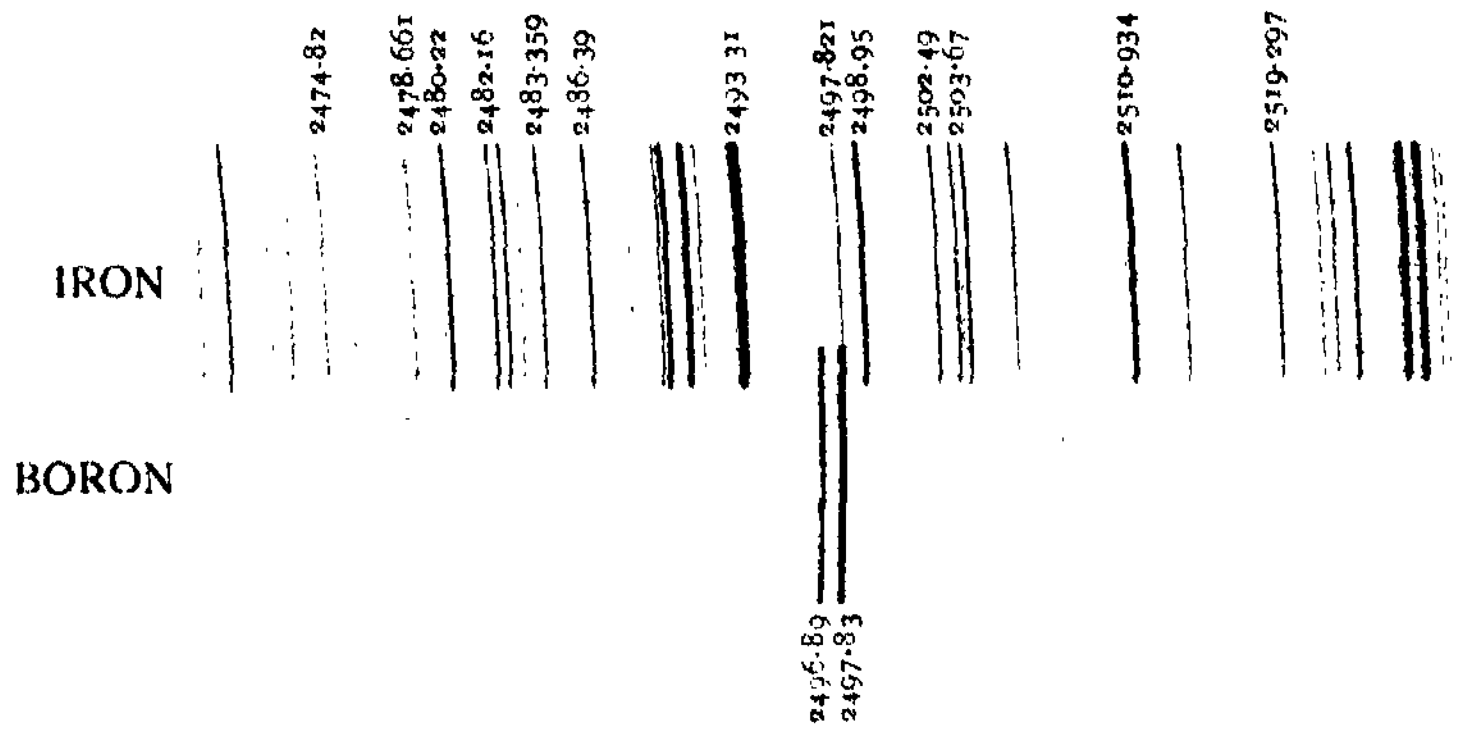
My reasons for selecting gold as the material for the clips were that it shows no lines near those in question of copper or aluminium; that it is a soft metal well adapted for clips holding hard bodies; that I had convenient blocks of it in a state of purity; and that all the lines of gold have been measured and mapped with accuracy.

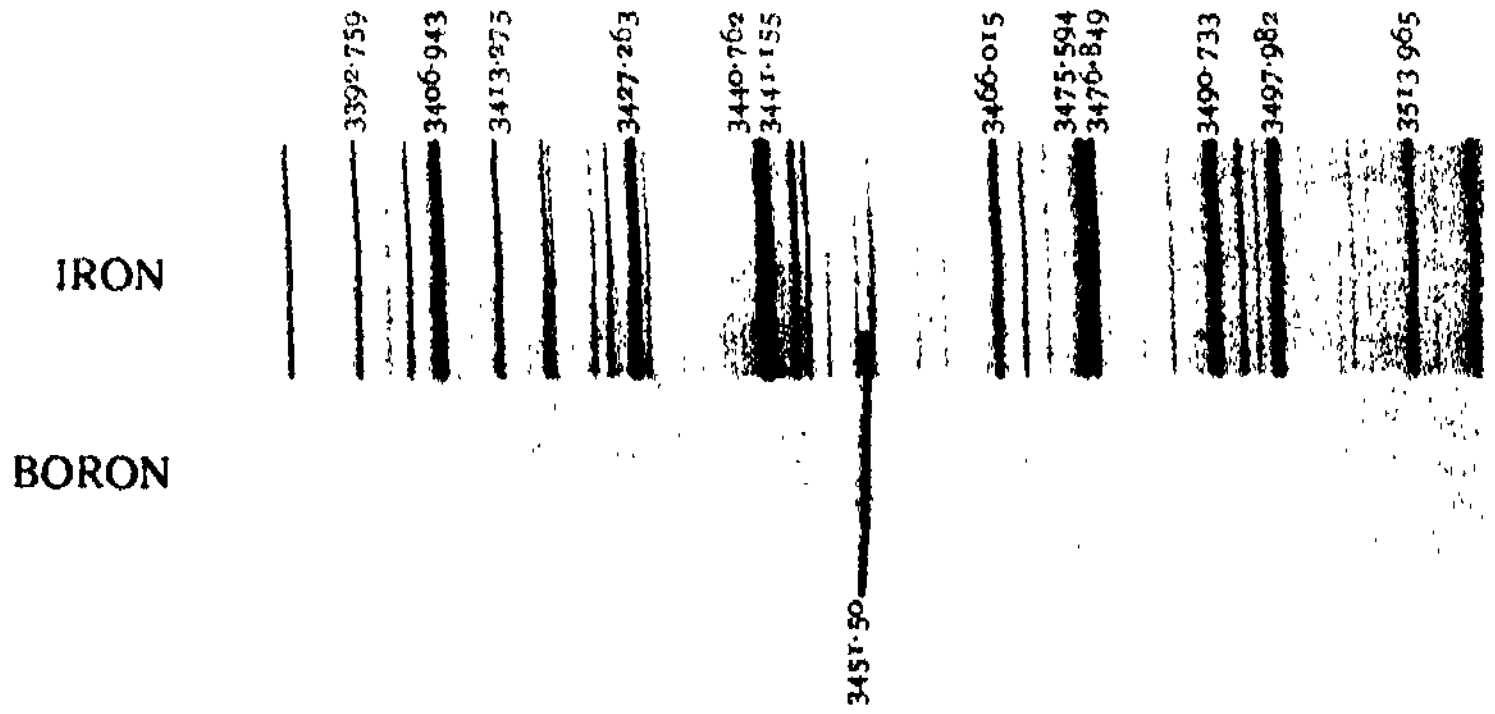
The poles of agglomerated boron after sparking for two hours—using gold clips—gave a spectrum in which no trace of copper lines could be seen, whereas a similar experiment in which melted boron was used in the gold clips showed decided lines of copper and traces of magnesium.

Another pair of lines occurred in the neighbourhood of wave-lengths 3082 and 3093 in the spectrum given by the melted boron, but not in that of the agglomerated plates. This pointed to other impurities in the melted boron. On comparing these lines with spectra of other elements it was soon discovered that they were two of the dominant lines of aluminium, 3082·275 and 3092·818.

Experiments were now made to see if by greatly prolonged exposures in the spectrograph other boron lines could be brought out. Melted boron, sparked for seven hours in gold clips, gave a photograph showing many additional lines, which, however, were for the most part ill-defined air lines; four, however, occurring between wave-lengths 3930 and 3970, were definite and sharp, although faint. These four lines might be due to boron, or to impurities, or they might be air lines. To ascertain if they were air lines, a control experiment was tried by photographing the spectrum of pure tungsten sparked for seven hours. Tungsten was selected as the metal to put in comparison with boron because in its spectrum there is a blank space where the four lines brought out by long exposure of boron occurred. Had any of these four lines been brought out by long exposure in the tungsten spectrum it would show that they were common to both and not peculiar to

THE BORON SPECTRUM





boron. Close examination of the tungsten spectrum showed no trace of the four lines. The two photographs were enlarged, and most of the lines in common were found to be air lines.

It having been proved that the four lines in question were not air lines, the remaining alternatives were—(*a*) they were boron lines, or (*b*) they were due to impurities in the boron.

To test the first hypothesis (*a*), that they were boron lines, several different specimens of boron, prepared by Dr. Weintraub and others, were examined in the spectrograph, and it was seen that the intensities of the lines varied considerably in comparison with known boron lines, being strong in some samples and almost absent in others. This pointed to hypothesis (*b*) as probably the true one, and a search was made for likely impurities having strong lines in the critical position.

Measurements were made of the four lines, and their wave-lengths were calculated from those of adjacent iron lines, and the figures left no doubt that they were traces of the calcium lines 3933·825 and 3968·625 and the aluminium lines 3944·160 and 3961·674, Rowland's wave-lengths. This was confirmed by comparison with my photographed maps of the calcium and aluminium spectra.

The result of my work on boron is to show that its photographed spectrum consists of three lines; that the 14 other lines given by J. M. Eder and E. Valenta, and the five other lines given by F. Exner and E. Haschek, failed to record themselves on my photographs, notwithstanding the excessively long exposures I gave in the attempts to bring out additional boron lines.

The collotype illustrations (Plate 1) are from the original negatives, and are entirely untouched. The grain of the process somewhat diminishes the sharpness of the lines.

To economise space and avoid unnecessary complications, I have given photographs of only that part of the spectrum adjacent to the boron lines. Had the whole spectrum been given as photographed, the length would have extended to more than 10 feet.

The upper half of each strip shows the iron lines used as standards, with their wave-lengths according to Rowland's latest measurements. The lower halves contain the boron lines, with their wave-lengths as calculated from the iron standards.

Colour-Blindness and the Trichromatic Theory of Colour Vision. Part III.—Incomplete Colour-Blindness.

By Sir W. de W. Abney, K.C.B., F.R.S.

(Received October 5,—Read November 2, 1911.)

The further the examination of partial colour-blindness is carried, the more apparent is the fact that what in Germany and elsewhere is called abnormal trichromatic vision is fully explained by the Young-Helmholtz trichromatic theory. Personally, I have not met with an instance of congenital colour-blindness in which a full explanation of the variations from normal vision is not offered by it.

In my last paper on this theory I promised to give another method by which the amount of colour perception deficiency could be determined quantitatively. The promise then made I will now fulfil. When a patch of white light is shown to any of the complete or incomplete colour-blind they recognize it as their own white, though not infrequently when they observe it in contrast with another colour the latter will miscall it. But, placed by itself, every person, colour-blind or not, will name it as white. If we place three slits in the spectrum, one in the red, where it has been shown that only the red sensation is stimulated, and another in the green, where the sensation curves tell us that all three sensations are excited, but the green mostly, and in excess of the other two, and the third in the violet, where only the red and the blue sensations are stimulated, we shall be able, by collecting the rays and altering the apertures of the slits, to make a mixture which will match the pure white when the two patches of light are placed side by side on a screen. The colour patch apparatus, which I have described in other papers, is perhaps the simplest apparatus with which to compare the mixed lights with the white. The normal eye will make his match which will be exact to him as his white. If a completely red-blind (the eye which sees a shortened spectrum) is asked if the match is satisfactory to him, he will say that it is. The completely green-blind will give the same answer. If the red slit* be completely closed the red-blind will see no difference in the match, for he has no red sensation which can be stimulated. If, however, a partially red-blind person be asked if the normal eye's match is exact, he will say it is not, but that the composite white is too green.

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* In this paper, as in others, the red, green, and violet slits are the slits through which the red, green, and violet rays pass.

By opening the red slit, or closing the green slit gradually, a point will be reached in which he says the match is exact. To the normal eye the match will appear red. If the widths of the slits be measured, both for the normal and also for the colour-blind, when the matches for hue to the one and the other are correct, and if both also match the respective luminosities of their composite light patches by opening or closing the rotating sectors placed in the path of the white beam which forms the white patch we have, when the positions that the slits occupy in the spectrum are known, a means of calculating the sensation deficiency in the partially colour-blind. If the deficiency in the colour-blind person be in the green sensation the normal eye's composite white will appear to him as too red. By opening the green slit gradually a width of slit will be found which makes the patch appear to the partially green-blind a match to the white. To the normal eye it will appear green, more or less pronounced, according to the degree of lack of response to the stimulation of the green perceiving apparatus in the eye. The slit apertures, and luminosity of the composite "white," are measured as before.

We will deal with the equations thus formed, which will be in the form of

$$a\ (\text{red}) + b\ (\text{green}) + c\ (\text{violet}) = m\ (\text{white}),$$

first of all without reference to m.

I will give two cases of this method of dealing with the equations.

The three slits were placed at S.S.N. 59·8 (the position of the red lithium line), at S.S.N. 38·3 (near the green Mg line), and at 8·5 (which is of less wave-length than G). A normal eye formed an equation to match the hue of white

$$100\ (\text{R.}) + 40\ (\text{G.}) + 55\ (\text{V.}) = \text{White}.$$

For convenience in calculation we can convert the equation into another in which G is 100

$$250\ (\text{R.}) + 100\ (\text{G.}) + 137\ (\text{V.}) = \text{White}.$$

The comparative luminosities of the rays passing through equal slits at the three points in the spectrum which they occupy were R. = 10, G. = 43, V. = 0·87. In the red there is only red sensation. In the green there are
R.S. G.S. B.S.
red, green, and blue sensations with luminosities of 21·18, 21·65, 0·1056 respectively, which make up the luminosity 43. In the violet ray the luminosity is 0·87 × 137, and is composed of 28 per cent. blue sensation and ·72 per cent. red sensation.

We will next see how much white the green ray contains. This is best done by changing the ordinates of the three sensations in the green into ordinates of the three sensation curves of equal stimulation, that is, when

Table showing the Luminosity of Spectrum formed by the Crater of the Arc with Horizontal Positive Pole and the Sensation Composition of the Different Rays. This light was used in the examples.

S.S.N.	λ.	Luminosity of spectrum.	Percentage composition.			Luminosity.			G.S. × 2·22.	B.S. × 110.
			R.S.	G.S.	B.S.	R.S.	G.S.	B.S.		
64	7217	0·5	100	—	—	0·5	—	—	—	—
62	6957	3·5	100	—	—	3·5	—	—	—	—
60	6728	8·7	100	—	—	8·7	—	—	—	—
58	6521	21·6	99	1	—	21·4	0·2	—	0·44	—
56	6330	48·3	95·5	4·5	—	46·1	2·2	—	4·9	—
54	6152	70	90·5	9·5	—	63·4	6·6	—	15·1	—
52	5996	84·5	84·2	15·8	—	71·7	12·8	—	30·4	—
50	5850	96·5	75	25	—	72·4	24·1	—	53·5	—
48	5720	100	67·12	32·9	0·030	67·1	32·9	0·030	73·0	3·3
46	5596	95	62·3	37·6	0·104	59·2	35·7	0·099	79·3	10·9
44	5481	85	58·1	41·74	0·158	49·4	35·4	0·134	78·6	14·7
42	5378	72	55·4	44·4	0·196	39·9	31·9	0·141	70·8	15·5
40	5270	56	51·57	48·2	0·224	29	27·0	0·126	59·9	13·9
38	5172	40·6	48·65	51·1	0·252	19·8	20·7	0·102	45·9	11·2
36	5085	27·3	46·08	53·5	0·42	12·6	14·6	0·115	32·4	12·65
34	5002	15·8	43·79	55·34	0·87	6·93	8·75	0·138	19·6	15·2
32	4924	8·9	42·17	56·13	1·7	3·76	5·00	0·152	11·1	16·7
30	4848	6·13	42·24	54·6	3·16	2·59	3·35	0·194	7·44	21·35
28	4776	4·66	44·36	50·54	5·20	2·06	2·35	0·242	5·22	26·6
26	4707	3·56	50·02	41·3	8·68	1·76	1·45	0·304	3·22	33·5
24	4639	2·69	58·56	28	13·44	1·58	0·75	0·362	1·66	39·8
22	4578	2·13	65·56	16·3	17·64	1·40	0·35	0·376	0·78	41·3
20	4517	1·8	70·72	8	21·28	1·27	0·14	0·383	0·31	42·1
18	4459	1·48	71·88	4·6	23·52	1·08	0·07	0·355	0·16	39
16	4404	1·28	72	2	25·76	0·92	0·03	0·330	0·07	36·3
14	4349	1·10	72	0·5	27·44	0·79	0·005	0·301	0·01	33·1
12	4296	0·98	72	—	28	0·7	—	0·275	—	30·3
10	4245	0·84	72	—	28	0·6	—	0·235	—	25·8
8	4198	0·72	72	—	28	0·52	—	0·202	—	22·2
6	4151	0·61	72	—	28	0·44	—	0·171	—	18·8
4	4106	0·5	72	—	28	0·36	—	0·140	—	15·4
2	4062	0·40	72	—	28	0·29	—	0·112	—	11·7
0	4010	0·3	72	—	28	0·22	—	0·084	—	9·2

the areas of the three sensation curves are equal. In these experiments the source of light was the arc light with a horizontal carbon for the positive pole. To make the green curve equal to the red curve the former had to be multiplied by 2·22 and the blue curve by 110. The three sensation curves thus multiplied give ordinates which when equal make white. Applying these factors to the components of the green ray we get

$$G. = \overset{\text{R.S.}}{9{\cdot}46} + \overset{\text{G.S.}}{16{\cdot}55} + 26 \text{ white.}$$

The 26 white evidently does not alter the hue of the mixture which goes to form white.

The equation when converted into luminosities, neglecting the white, becomes

$$\underbrace{\overset{\text{R.S.}}{2500}}_{\text{R.}}+\underbrace{\overset{\text{R.S.}}{946}+\overset{\text{G.S.}}{1655}}_{\text{G.}}+\underbrace{\overset{\text{R.S.}}{66}+\overset{\text{B.S.}}{25}}_{\text{V.}}=\overset{\text{R.S.}}{3512}+\overset{\text{G.S.}}{1655}+\overset{\text{B.S.}}{25}.$$

In the case of a red-blind his mixture to match his white was

$$100\,(\text{R.})+27\,(\text{G.})+45\,(\text{V.})=\text{White.}$$

Again, making G. = 100, we get

$$\overset{\text{R.}}{370}+\overset{\text{G.}}{100}+\overset{\text{V.}}{167}.$$

Working this out into the normal luminosity of the sensations we get

$$\underbrace{\overset{\text{R.S.}}{3700}}_{\text{R.}}+\underbrace{(\overset{\text{R.S.}}{946}+\overset{\text{G.S.}}{1655})}_{\text{G.}}+\underbrace{(\overset{\text{R.S.}}{104}+\overset{\text{B.S.}}{41})}_{\text{V.}}$$

or

$$\overset{\text{R.S.}}{4750}+\overset{\text{G.S.}}{1655}+\overset{\text{B.S.}}{41}.$$

To the same amounts of green the amount of red in the normal is to the red of the colour-blind as

3512 to 4750;

that is, the colour-blind has only 0·75 the normal R. sensation.

The figure obtained by the luminosity method described in my last paper was the same, viz., 0·75 R.S.

It is to be observed that the result is obtained by considering the mixture from a normal eye point of view. Presently we shall see that this is a perfectly legitimate aspect.*

In regard to the white in the green ray, it is present to the colour-blind as it is to the normal vision, though it is different in hue, but like the white he matches, and consequently differs in luminosity, but as it has, as in the case of the normal eye, no effect on the resulting hue, it is not taken into account. It has to be remembered that to get sensation curves of equal areas for the colour-blind, the factors have to be increased for the green curve in the case of partial green-blindness, and a factor has also to be introduced for the red curve in the case of partial red-blindness.

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* The mixtures are first found by measuring the apertures of the slits when a match to white is made by the colour-blind. It is then converted into luminosities according to the normal eye scale. Whichever sensation is in defect has really to be multiplied by a factor, and that factor is ascertained by making (say) the green sensations equal as just given.

Another case is one of green-blindness, which will be the second example of this method of treating the equation. The observer Y is a case of interest, as he has often been quoted as an example of abnormal trichromatic vision.

The measures were taken in the presence of Dr. W. Watson, F.R.S., with the colour patch apparatus. The equation of Y for white was

$$98\,(\text{R.}) + 100\,(\text{G.}) + 67\,(\text{V.}) = \text{White}.$$

Treating this equation as before, we find that to a normal eye the equation in luminosities becomes

$$\begin{array}{ccc} \text{R.S.} & \text{G.S.} & \text{B.S.} \\ 1926 + & 1655 + & 16. \end{array}$$

In this case, to get the green sensation present in the colour-blind eye, we must *divide* Y's R.S. (red sensation) by the normal red sensation or $1926/3512 = 0{\cdot}54$ closely of normal G.S. Y's luminosities at five different places in the spectrum (see previous paper for method) gave a mean value of 0·58 G.S.

This shows that the "white" equations treated this way give trustworthy measures of deficiencies where the factors are not very small.

[I will here interpolate a caution as to the luminosity method of getting the factor of deficiency where there is a suspicion that the macula lutea is very highly or very little pigmented. It is safe in such cases to confine the luminosity measures to S.S.N.'s greater than 42 or 44. With lower S.S.N.'s the question of pigmentation may cause a difference in the factors obtained. The last case, it may be mentioned, is an example of this. The pigmentation of Y's macula lutea was far *above* the ordinary pigmentation.]

This method of treatment of the white equations is, then, exact within limits. So long as the factor for the sensation is not below 0·5, it may be followed, but below that point there may be erroneous estimates derived from the calculation. I have shown elsewhere that the normal eye cannot detect within 2 per cent. of excess of a colour matched to a white, and guard had to be taken against this in forming colour equations, to ascertain the spectrum colour sensation curves for the normal eye. There is reason to believe (I will not now enter fully into details on which I base my belief) that for small sensation factors a much larger quantity of colour may be added to this white, and of white to the colour, than can be added by the normal eye without detection. It has already been pointed out that, to a completely red-blind, the match to the normal eye is satisfactory, although it is just as satisfactory to him if the red slit be closed. Indeed, any amount of red may be added to his white without altering the match. We can understand that, with an eye which only has, say, 0·05 R.S., an almost equal amount of red might be added to the white and not be perceived. As the factor increases, the amount of white that can be added to the red, or of red to the white, without altering the hue, will be less—and so also with the green sensation. It seems that the ordinates of a curve that may represent the amounts that can be added may probably be calculated from the ordinates of an hyperbola.

Whatever may be the reason of the want of perception of the added colour we know that the want exists, and the second method of treating the equation gets over any difficulty on this account. The method is a combination of the first method with that of the luminosity method. If when the white is matched in hue by the colour-blind, he is also required to make a determination of the luminosity of his composite white, and if the normal eye also takes a measure of the luminosity of the colour-blind composite white, or takes a measure of the luminosity of his own composite white, there are sufficient data with which to calculate the sensation deficiency. It should be noticed that the luminosity of a composite white against a pure white is very easily measured. There is no difficulty in it, though it may exist to some observers when the luminosity of a *colour* against white has to be determined.

We will suppose that the following equation has been made by a green-blind :—

$$a(\text{R.})+b(\text{G.})+c(\text{V.}) = p^\circ \text{ of sector to the colour-blind,}$$

and that to the normal eye it has a luminosity of m°. It is only necessary to take into account the luminosities of the red and green sensations, since those of the blue sensation are very small compared with them.

Let us turn the colours into sensation luminosities, this time not calculating out the white in the green ray, and the equation becomes to the normal eye

$$\overset{\text{R.S.}}{a'}+\overset{\text{G.S.}}{b'} = hm,$$

h being the factor which makes $m = (a'+b')$. Using h for the green-blind equation we have hp°, but to the colour-blind p° is dependent on the area of his total luminosity curve, which is smaller than the area of the normal luminosity curve of the spectrum.

Let A be the area of the normal luminosity curve, and A′ the area of the colour-blind luminosity curve.

To make hp° balance the composite white to the normal eye the left-hand members of the equation must be multiplied by A/A', and calling x the factor of the green deficiency for the colour-blind, we get

$$a'\frac{A}{A'}+b'x\frac{A}{A'} = hp.$$

For our purpose we must convert the equation into the "language" of the normal eye : p would become $pA'/A = m$.

We can multiply both sides by A'/A and we get

$$a'+b'x = hp\frac{A'}{A},$$

If the value of A be 10, *i.e.*, $(\overset{\text{R.S.}}{6{\cdot}8}+\overset{\text{G.S.}}{3{\cdot}2})$,* A' is $\overset{\text{R S.}}{6{\cdot}8}+\overset{\text{G.S.}}{3{\cdot}2x}$,

$$A'/A = (0{\cdot}68+0{\cdot}32x),$$

$$x = \frac{0{\cdot}68hp-a'}{b'-0{\cdot}32hp}.$$

If the deficiency were in the red sensation

$$x = \frac{0{\cdot}68hp-b'}{a'-0{\cdot}32hp}.$$

The value of h may be determined, we said before, by the normal eye measuring his composite white against the same white patch which the colour-blind matched.

It will be noticed that x is determined regardless of the true amounts of R.S. and G.S. on the left-hand side of the equation.

The following is an example of what may be called a glaring case of an untrue equation being formed by a nearly completely red-blind person (S). The mean of two of his equations was

$$30\,(\text{R.})+16{\cdot}75\,(\text{G.})+12{\cdot}75\,(\text{V.}) = 27{\cdot}2^\circ \text{ of sector in white.}$$

We may neglect the luminosity of the blue sensation and use only the red and green.

Converting the above into luminosities of R.S. and G.S. (in this instance not taking away the white which is in the green ray, as all its components of red and green sensations are required), viz., $\overset{\text{R.S.}}{21{\cdot}18}$ and $\overset{\text{G.S.}}{21{\cdot}65}$ (see *ante*), and, having found from a normal vision equation that $h = 41$, we get

$$\overset{\text{R.S.}}{300}+\underbrace{(\overset{\text{R.S.}}{355}+\overset{\text{G.S.}}{365})}_{\text{G.}} = 27{\cdot}2\times 41\,(0{\cdot}68x+0{\cdot}32),$$

or

$$\overset{\text{R.S.}}{655x}+\overset{\text{G.S.}}{365} = \overset{\text{R.S.}}{75{\cdot}8x}+\overset{\text{G.S.}}{357}.$$

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* These numbers are derived from the luminosity sensation (R and G) curves of the light used in these measures.

From this we get $x = 0{\cdot}08$ nearly,

or S. possesses about 0·1 of the normal R.S.

Using the first method of treating the equation he would have been supposed to have 0·8 R.S. His R.S. calculated by the luminosity method given in my last paper was 0·1 closely.

A case of green-blindness (Wn.), which gave a fairly large deficiency by the luminosity method, is now given. His equation to white was

$$30\,(\mathrm{R.}) + 32\,(\mathrm{G.}) + 39\,(\mathrm{V.}) = 23 \text{ white.}$$

At the same time, and using the same comparison white beam, a person having normal vision found an equation which gave a factor h for the white* of 67.

Applying this factor to Wn.'s equation, we get as the luminosity equation

$$\begin{array}{l} \quad \text{R.S.} \quad \text{G.S.} \\ 978 + 691x = 1048 + 493x, \\ \qquad\qquad x = 0{\cdot}35 \text{ of normal G.S.} \end{array}$$

His factor of G.S. obtained by the luminosity method was about 0·33.

If we treat Wn.'s equation by the first method, we get a factor of 0·54.

These two cases confirm what has been said as to non-recognition of white or colour when added above the 2-per-cent. limit.

When there is a large deficiency of a colour sensation, the composite white such colour-blind persons would form to match the comparison white indicates to the normal eye the likelihood of the deficient sensation being added without being perceived. To the normal eye the composite white of the largely deficient green-blind appears as a slightly pale purple, and of the largely deficient red-blind a slightly pale sea-green.

[In the examples given, the position of the green slit is not the best one to use, *as the ray,* besides the white, contains both *green and red sensations.* The ideal position is that the ray which passes through this slit should only be composed of white and green sensations. The position on my standard scale with the arc light and horizontal carbon is close to S.S.N. 36.

In any case it is preferable that the ray should contain white, green, and a little blue sensations rather than white, green, and red sensations, as the latter imposes a limit on the green sensation factor. In the position S.S.N. 38·3 which the slit has occupied in the above examples the limit of the factor is about 0·26 G.S. For the red deficiency there is no limit when using that position.]

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* It is not possible so far to always have an equally luminous white day by day; it varies according to circumstances, but remains constant during the time the instrument is working, no part of the adjustments being altered. I am in hopes that any variation in this comparison light will be got rid of, as it would be a great saving in time.

A favourite plan in Germany for a semi-quantitative measure of colour sensation deficiency is that which I believe originated with Lord Rayleigh. This method is one of mixing red and green to match the sodium D light of the spectrum. There are special instruments extant for this purpose, and note is directed to be made of the quantities and intensities of each colour which is required to give a match to this light, but I am unaware of any means by which the factor of deficiency can be ascertained, though it is now easy to give such a scale when the positions of the red and the green in the spectrum are known.

If we place two slits in the colour patch apparatus in the same positions that we have already used in the red and the green, we can form a very close approximation to the sensation deficiency by the match made of the D light. The match made will be of the same *hue* as the D light when a little white is added, for there will be white mixed with the match and the white will be the colour of the light forming the spectrum. In a communication I made to the Royal Society, and which appears in the 'Proceedings,' I called attention to the fact that from the scarlet to the yellow the addition of white to a colour made its hue yellower, and from the blue-green to the green the same "yellowing" of hue was apparent.

In matching the D light with a green (every green contains white) and a pure red the true proportion of R.S. and G.S. in the match will not be quite identical with those in the D light itself. If the colour to be matched be at S.S.N. 48·7 of my scale, which is where the red and green curves of equal areas cut, there will be no difficulty experienced, since at that point no change in hue is found when white light is added to it. So far this applies to the arc light.

If, however, a light such as the paraffin light is employed as the source for the spectrum, the red and green curves of equal areas will cut very close to D in the spectrum, and the white light existing in the green ray, when calculated out, as I have done it for the arc light, will be very nearly the hue of the D light, so that there will be no shifting of hue. It is necessary to mention this, as if the match is to be used for ascertaining colour sensation deficiency, the sensation curves for the light source must be employed in the calculations.

A gauge of accuracy of measurement is the closeness with which the mixture of red and green made by a normal eye shall give the hue and the proportion of sensations existing in the D light.

My own mean equation for the D light with the slits in the same position as before is

$$447\,(\mathrm{R.}) + 100\,(\mathrm{G.}) = \mathrm{D\ light.}$$

This when worked out with luminosities gives a percentage value of

$$\begin{matrix}\text{R.S.} & \text{G.S.}\\ 77 & +\;23,\end{matrix}$$

as contained in the mixture neglecting the white. This is very slightly (0·3) less red than is contained in the D light, and is to be accounted for by the white existing in the green ray.

There is in these D equations, as in the equations for white light, the same possibility of their failure when the sensation factor is small owing to the non-perception of added colour,* but if the luminosity of the D light (or other selected ray) be measured against the mixed colours, the difficulty, as before, vanishes.

The methods described have depended on measurements made in the spectrum itself, but I wish to call attention to another source of measures which can be used without the spectrum apparatus. It is true that its accuracy in the first instance depends upon measurements made in the spectrum, but when once made the amount of colour sensation can be determined without further reference to it. I allude to the colour-disc equations. Given three discs of equal diameter (say 4-inch), capable of interlacing and of being rotated, one of which is painted with a red pigment, another with a green pigment, and the third with a blue pigment, by altering the angles of the interlacing discs a grey can be formed on their rotation, and this can be matched by a white and a black disc of say 6 inches diameter also rotating on the same spindle. Of course there is nothing new in this method, but I venture to think that the method of treating the equations given by the colour discs will be found new in some details. I would point out that colour discs can be used *in any light*, but that to be really useful for calculation the kind of light should be known. The colours of the discs themselves are the only part of the apparatus which requires careful measurement, and this must be done in the spectrum. The composition of the colours must be ascertained in terms of the three-colour sensations, and the luminosity of the colours must also be known. The former and the latter will both vary according to the nature of the light in which they are viewed. We may proceed in ascertaining the composition of the pigment colours by the method I give in my paper, pp. 351—353, in the 'Phil. Trans.,' 1905.†

The compositions of the pigments are there given for the light of the electric arc, but when the luminosity curve of the spectrum of any other light is known the sensation luminosities in the pigment colours can be at once calculated from the table at p. 344, or from that given in this paper, when the amount of each ray which is reflected from the pigmented surface has been measured. Such a method also gives the luminosities in terms of the total white light used to form the spectrum. This is an exact method, but a somewhat long one, but it tells more about the pigment than is necessary to know for the purpose that is in view. All we require to know, as said before, is the sensation luminosity composition and the total luminosity. The former we can arrive at in a very simple manner.

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* I have often seen very widely different equations formed by the same observer when matches of the D light are made.

† "Modified Apparatus for the Measurement of Colour."

Let us place a square piece of the pigmented paper in the colour patch apparatus, and side by side with it an equal square of a white surface. Let the pigment patch be illuminated by the light in which the discs are to be used, say, gaslight, incandescent light, etc. (daylight is out of the question, as it is so variable in quality), whilst the other is illuminated by the light coming through the three slits in the spectrum, as has already been described. By placing a rod in the path of the beams the two illuminations may be separated, but can be caused to touch one another. All we have to do is to match the colour of the pigment as seen in the light by which it is illuminated with the mixture of the rays coming through two or three of the slits. Having done this, the width of slits must be measured as before. When converted into luminosities, and the luminosities into the respective sensations existing in the rays, the amount of the sensations stimulated by the pigment can be calculated.* By making the patches equally bright the relative luminosities of the pigments compared with white can also be ascertained with great exactitude if the pigmented paper is removed and a second square of white paper is substituted for it and the light itself matched. The sensation values of the three coloured discs for the light in which they are to be viewed will now be known, as also the luminosity.

To use the discs to give true equations the illumination must be that of the same kind of light in which these are determined. It will not do, for instance, to use the values obtained for the arc light in daylight or in gaslight. If an incandescent light (say) is used for the illumination of the pigment during measurement the discs must be rotated in the same light. Stress is laid on this, as it is not uncommon for those using colour discs to be lax as to the light they use.

The three discs are placed on the spindle of the whirling apparatus (I use a small motor for the purpose) with the interlaced black and white discs behind them. The coloured discs are altered till a grey is obtained which matches the grey of the rotating black and white discs.* The angular apertures of the exposed parts of the several discs are all measured and the values recorded as

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* It may be stated that the two methods of finding the sensations are practically identical.

$$a \text{ red} + b \text{ green} + c \text{ blue} = m \text{ white} + (360 - m) \text{ black}.$$

The amount of white reflected from the black is measured, and if n be the factor the white becomes $m + (360 - m)\,n$.

It is essential in some cases that both the greys should be of exactly the same brightness. (It need scarcely be said they should be identical in hue.) Everything depends, for a true determination of the amount of colour-blindness, on the true matches being made.

It may here be emphasised that both luminosity and sensation composition will vary in every light, so that exactitude of match in any light but that in which the measurements have been made is labour thrown away.

I will now give examples of the mode in which the equations should be treated. The treatment will be identical with that just given. The light in which the rotation of the discs was made is the naked arc light, and all the measures were made in that light.

The following is the equation which I made with the discs:—

$$126 \text{ red} + 144 \text{ green} + 90 \text{ blue} = 79 \text{ white} \qquad \text{(i)}$$

and the black reflected just 5 per cent. of white light, so that the equation on the right-hand side becomes

$$79 + 281 \times 0·05, \quad \text{or} \quad 93°.$$

The composition of the vermilion-red I had found to be (in terms of the luminosity of the whole spectrum, and which equalled in area 866 on an empyric scale)—

	R.S.	G.S.	White.	
	142·5	+16·5	+ 53,	(ii)
the emerald green was	31·8	+60	+263,	(iii)
and the blue	2·34+	1·56+	34·2.	(iv)

Multiplying the equation (i) by the appropriate factors in (ii), (iii), and (iv), and dividing by 360° we get

R.S.	G.S.	B.S.	White.
49·9+	5·8+	0	+18·55,
12·7+	24·0+	0	+105·2,
	0·6+	0·4+	8·55,

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* It is well that the matches should be made with the light falling perpendicularly on the discs and the observer being as nearly as possible facing them.

which when added together give

$$\begin{array}{cccc} \text{R.S.} & \text{G.S.} & \text{B.S.} & \text{White.} \\ 62{\cdot}6 & +\,30{\cdot}4 & +\,0{\cdot}4 & +\,132{\cdot}3 \end{array}$$

Dividing this equation by 866 we get the sensation-luminosities for the mixed colours

$$\begin{array}{ccccc} \text{R.S.} & \text{G.S.} & \text{B.S.} & \text{White.} & \\ 0{\cdot}0725 & +\,0{\cdot}0351 & +\,0{\cdot}0005 & +\,0{\cdot}1527 & =\,0{\cdot}2608. \end{array}$$

The ratio of R.S. to G.S. is 67 to 33, which is closely that obtained from the spectrum equation, so that my equation derived from the discs may be taken as the normal vision equation.

We do not *need* to refer to the right-hand member of the equation, but if we take it as 93 the luminosity of the white exposed is 93/360 of 1, or 0·259.

It will be seen that the luminosities agree to within the third place of decimals.

When a colour-blind person is tried in the same light his equation is

$$210 \text{ red} + 100 \text{ green} + 50 \text{ blue} = 77.$$

Taking the luminosities of the red, green, and blue as before we get, when multiplying them by the equation numbers (ii), (iii), and (iv) ÷360.

$$\begin{array}{cccc} \text{R.S.} & \text{G.S.} & \text{B.S.} & \text{White.} \\ 91{\cdot}94 & +\,26{\cdot}6 & +\,0{\cdot}22 & +\,108{\cdot}7. \end{array}$$

Dividing by 866, as before, we get

$$\begin{array}{ccccc} & & & & \text{Total} \\ \text{R.S.} & \text{G.S.} & \text{B.S.} & \text{White.} & \text{luminosity.} \\ 0{\cdot}1062 & +\,0{\cdot}0307 & +\,0{\cdot}00025 & +\,0{\cdot}1253 & =\,0{\cdot}2624. \end{array}$$

R.S. is to G.S. as 114·2 to 33, the normal equation being as 67 to 33.

The degree of red blindness is given by 67/114·2 or 0·58 R.S.

We may now examine the right member of the equation, which is the white in the outer two discs of black and white. It is 77, and with the light reflected from the black becomes 91, and 91/360 = 0·2527.

We may now subtract the white of the left-hand member from it, and we get the following equation left:—

$$\begin{array}{ccc} \text{R.S.} & \text{G.S.} & \text{(R.B., white).} \\ 0{\cdot}1062x & +\,0{\cdot}0307 & =\,0{\cdot}1274, \end{array}$$

where x is the R.S. factor.

As in the second method of using the spectrum equations for the colour blind, we multiply 0·1274 by $(67\,x+33)$, as $(67+33)$ is the normal relation of R.S. to G.S.

This worked out gives $x = 0{\cdot}54$ R.S. Another colour-blind makes the same equation match with 72 white.

Proceeding in the same manner we get

$$\overset{\text{R.S.}}{0\cdot1062x} + \overset{\text{G.S.}}{0\cdot0307} = \overset{\text{R.S.}}{0\cdot0768x} + \overset{\text{G.S.}}{0\cdot0379}.$$

$x = 0\cdot24$ of the normal luminosity.

We see, then, that where there is a deficiency in the mixtures due to causes already pointed out, the degree of colour-blindness can still be calculated out, always supposing that black and white mixture is to the observer a perfect match to the inner grey given by the discs.

The question of other illumination need not be entered into by examples. They would be carried out in exactly the same manner as that indicated. The use of colour discs to form equations, as before said, has long been known, but I venture to think that the method of using the equations in the manner indicated gives them a new value. As the equations from these discs give such accurate results, it may be that those interested in colour vision might use them. Let the light used to view the rotating discs when matched with the outer grey be, say, the light of an incandescent mantle burner, in front of which is a palish yellow glass or cell containing potassium chromate saturated solution, then any difficulty about the amount of pigment in the macula lutea will be reduced to a minimum. If the three colours be matched by a red, green, and blue* (passing through three slits) of known luminosities and known sensation composition when they (the pigments) are illuminated by this same light, it would not be impossible to make a scale for both red and green blindness. If the angles of the three colours in the discs be calculated out for the different degrees of colour-blindness, say, for 0·1, 0·2, 0·3, etc., red sensation, and the same for the green sensation, and also the angle which the whites in the outer ring should have for the same degrees of colour-blindness, a miniature set of 20 discs could be prepared, each representing the 20 factors of blindness. By a not very difficult arrangement all the discs might be rotated together, and the colour-blind person would be asked to pick out that one which seemed to him the most perfect match in colour and brightness. At once the examiner would be able to ascertain the factor (to the first place of decimals) of the deficient sensation.

I have mentioned this idea, as it is not everyone who has a complete spectrum apparatus for forming equations, but he might obtain the colour discs from some of the firms which supply ophthalmic apparatus if enquired for.

I may finally mention that colour equations to match a yellow pigment can be formed in the same way as for the white, but it entails not only a black disc in the outer ring, but also a white disc, for the mixed colours in the inner discs contain as a rule more white than does the yellow. It was my intention to have mentioned in this communication the question of the colours which the incompletely colour-blind see, or say they see, but, as the foregoing results are based on measures of colours and not on the colours themselves, I have reserved this subject for possibly another communication.

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* The blue will probably not be required.

A Chemically Active Modification of Nitrogen produced by the Electric Discharge.—II.*

By the Hon. R. J. Strutt, F.R.S., Professor of Physics, Imperial College of Science, South Kensington.

(Received October 11,—Read November 9, 1911.)

1. *Behaviour with Oxygen and Hydrogen.*

It was noticed previously[†] that oxygen destroyed the nitrogen afterglow. There is no doubt whatever that this is a positively destructive effect, as opposed to a mere dilution. For if a stream of oxygen is admitted through a stopcock into the stream of glowing nitrogen, the glow is extinguished: replacing the oxygen with an equal (inert) nitrogen feed, the nitrogen glow reappears, only slightly weakened by dilution.

No oxidation of nitrogen accompanies the destruction of the glow. The mixed gases were passed through a U-tube cooled in liquid air for half-an-hour. No deposit could be seen in the tube. The condensed gases from the U-tube (if any) were collected through a Töpler pump on warming up. Nothing was collected beyond about ½ c.c. of nitrogen, which was presumably derived from leakage, since liquid air could not have condensed it.

Any oxide of nitrogen except nitric oxide would be completely collected in the cooled tube. Nitric oxide, if it had been formed, would have been further acted on by the active nitrogen, forming nitrogen peroxide, which would have been at once detected.[‡] It can only be concluded that the destruction of active nitrogen by oxygen is catalytic, and analogous to its

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[*] In continuation of the Bakerian Lecture for 1911, 'Roy. Soc. Proc.,' A, vol. 85, p. 219.

[†] *Loc. cit.*, p. 224.

[‡] *Loc. cit.*, p. 227.

destruction by cupric oxide.* These experiments seem to prove that active nitrogen plays no part in the oxidation of nitrogen by the electric spark, as for instance in preparing argon.

Hydrogen, so far as the luminous phenomena are concerned, merely dilutes the active nitrogen, without exhibiting its own spectrum.† The issuing gases are neutral to litmus paper, there is therefore no formation of ammonia, and in all probability no chemical action at all.

2. *Reaction with Nitric Oxide.*

Nitric oxide led into active nitrogen combines with it, giving rise to a greenish-yellow flame with continuous spectrum, and forming nitrogen peroxide.‡ At the time when the former paper was written, it had unaccountably escaped me that this flame is *identical with that observed when nitric oxide unites with ozone* (the air afterglow).§ Evidence of this from the spectroscopic side is of necessity not very cogent, but the continuous spectra of the two have the same range of wave-lengths. When, however, the flames are produced side by side for comparison, the peculiar tint is seen identically in each, so as to satisfy the mind completely.

The same flame is developed, though less conspicuously, when nitrogen peroxide is led into the active nitrogen. The nitrogen peroxide used was prepared by heating lead nitrate, and purified by liquid air condensation. Conditions under which I have observed this flame may be summarised thus—

(1) Ozone mixed with nitric oxide.
(2) Ozone mixed with nitrogen peroxide.
(3) Active nitrogen mixed with nitric oxide.
(4) Active nitrogen mixed with nitrogen peroxide.
(5) Nitric oxide fed into Bunsen flame.
(6) Nitrogen peroxide fed into Bunsen flame.

If the yellowish-green luminosity is regarded as due to the vibration of some particular atomic or molecular system, it seems likely that this system is the nitrogen peroxide molecule.

In cases (2) and (4) nitric oxide is certainly absent, whereas in all cases nitrogen peroxide is present, either originally or as the product of a reaction.

In cases (1) and (2) nitrogen pentoxide is formed. But in (3) and (4) it is absent, the product of reaction being the peroxide.

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* *Loc. cit.*, p. 226.

† Helium fed into the glowing nitrogen behaves similarly.

‡ *Loc. cit.*, p. 227.

§ 'Phys. Soc. Proc.,' Dec. 15, 1911, vol. 23, p. 66.

Assuming that the greenish-yellow glow is due to the nitrogen peroxide molecule, it must be supposed that in case (4) it is merely stimulated by the energy of the active nitrogen, without chemical change. In the other cases, chemical action occurs and may assist the stimulation. This is quite parallel to what happens in the case of cyanogen.*

The reaction with nitric oxide has been made use of to estimate the percentage of active nitrogen in the total nitrogen leaving an electric discharge. The method was to add excess of nitric oxide to the glowing nitrogen, and to weigh the resulting blue substance which is condensed out from the gases by liquid air.

The blue substance is regarded as nitrogen trioxide, N_2O_3. It is formed by two successive reactions. The first of these results in the formation of nitrogen peroxide,

$$2NO + N = NO_2 + N_2.$$

Nitrogen peroxide then combines (at a low temperature) with more nitric oxide, to form the blue substance,

$$NO_2 + NO = N_2O_3.$$

Thus 14 parts by weight of active nitrogen yield 76 parts of the blue substance. The reaction is therefore very advantageous in respect of the large mass of the product.

The N_2O_3 was weighed in a U-tube provided with glass stopcocks. It was found that some excess of NO was apt to be condensed, in solution or otherwise, along with the N_2O_3. To get rid of this the U-tube was allowed to warm up to about −50° C. and the NO pumped off. No sensible evaporation of N_2O_3 occurs at this temperature. The tube was then closed, and weighed at the ordinary temperature.

In a typical experiment, 540 c.c. of nitrogen were passed through a vacuum tube and then mixed with nitric oxide. The total volume of the latter passed was 460 c.c. It was, therefore, present in ample excess. The weight of N_2O_3 collected was 90 mgrm.

Thus the percentage of nitrogen converted to the active form was 2·46. Other determinations gave similar results.

This is a much higher value than the 0·5 per cent. obtained in my former experiments, in which active nitrogen was determined by phosphorus absorption.† The conditions cannot be kept very constant, but the inevitable variations will not explain this great difference. Nor is it easily explained by any different view of the chemical changes involved. I am inclined to attribute it to an action of phosphorus in destroying active nitrogen, similar to that of oxygen as described above. On this view, active nitrogen, on coming into contact with phosphorus or its vapour, in part combines and is in part destroyed without combination. The former portion alone is estimated, and the result is necessarily low.

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* *Loc. cit.*, pp. 226, 228.

† *Loc. cit.*, p. 223.

3. *Action on Phosphorus.*

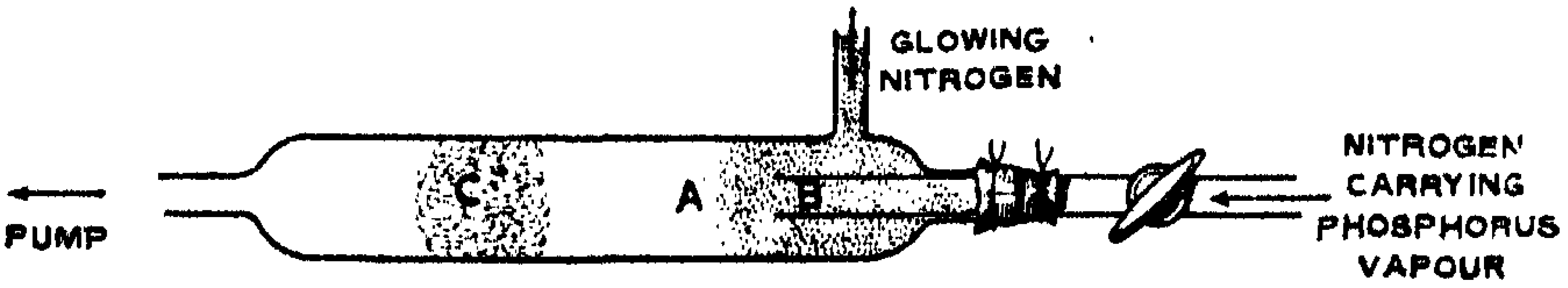
In this connection some very peculiar phenomena may be recorded, of which, however, I can offer no satisfactory interpretation. For the Royal Society Soirée in May last a large vessel was prepared, into which a jet of glowing nitrogen was delivered from a vacuum tube. A large power air pump maintained the vacuum. The vessel filled up in a few seconds with glowing nitrogen, giving a magnificent orange light. If the discharge was turned off this luminosity faded away, partly owing to its natural decay and partly to replacement with non-excited nitrogen entering the vessel. Frequently, however, the following effect was noticed: About 1½ or 2 seconds after the discharge was turned off a new luminosity was seen entering the vessel from the jet, much whiter in colour, and giving a continuous spectrum. This expanded, nearly filling the vessel, and then died down to nothing. Its duration may have been about 2 seconds. There was a well-marked dark cone about the jet, showing clearly that the luminosity was due to some reaction between the gas already present, which had been subjected to the discharge, and that entering at the time, which had not.

After some trouble, the proximate cause of this effect was found to be as follows: The nitrogen stream had been purified from residual oxygen by passing through a tube filled with chips of phosphorus, and thus carried phosphorus vapour with it into the vacuum tube. While the current is passing, this phosphorus at once combines with nitrogen in the discharge tube, and none of it enters the large vessel. When the discharge stops, phosphorus vapour comes through and reacts with the active nitrogen remaining in the large vessel. The reaction produces the mysterious jet of whitish luminosity; but the difficulty remains, why does not this action occur at once instead of hanging fire until the nitrogen in the large vessel has nearly lost its orange glow, and therewith (as all the other phenomena had led one to suppose) its active properties?

This "hang fire" may be better examined by the following modification of the experiment, which admits of continuous observation:—

The experimental tube is as shown. The nitrogen glow dies out about the point A. An independent jet of nitrogen, saturated with phosphorus vapour, but not activated, enters through the jet B into the glow. As soon as this jet is turned on, a flame with a continuous spectrum appears at C, separated by a considerable dark interval, not only from the jet, but from the boundary of the nitrogen glow.

If the jet B is pushed forward to the point C, the flame burns at its mouth, and continues to do so even if it is pushed considerably further, though in this latter case the intensity is progressively diminished.



The experiment seems to prove that after activated nitrogen has completely undergone the change which gives rise to the glow, some second change must occur before it is prepared to combine with phosphorus vapour. Thus the phenomena are complicated, and it seems doubtful if the current atomic or molecular conceptions of chemistry will suffice to describe them.

4. *Electrical Properties of Glowing Nitrogen.*

Glowing nitrogen is found to possess very marked electrical conductivity. If two electrodes are immersed in it, it is found that a current able to produce a large deflection on an ordinary high resistance galvanometer can be sent between them by a single battery cell. Without attempting elaborate quantitative statements, it may be said generally that the conductivity is of the same order as in a salted Bunsen flame.

The question now presses for answer: Where do the ions thus present in the glowing nitrogen originate? Do they come from the original discharge, or are they generated afterwards, in the course of the changes occurring in the glowing nitrogen?

In the first place, it is to be noted that no conductivity of this order can be observed in the issuing gases when air* or oxygen or hydrogen is substituted for nitrogen. There is, indeed, ionisation surviving from the discharge, but though conspicuous to electrostatic methods of measurement, it falls far short of what can be observed on an ordinary galvanometer. Large conductivity is peculiar to nitrogen pure enough to give the afterglow. Moreover, the testing electrodes must be immersed in the glowing gas. If they are situated beyond the termination of the glow, the galvanometer is not deflected.

These observations decidedly suggest that the large formation of ions occurs in the afterglow, and that they are not derived straight from the original discharge. But the following experiment seems conclusive. Oxygen destroys the afterglow (see above, § 1). Now we cannot suppose that the introduction of oxygen would destroy a pre-existing ionisation in the nitrogen. Yet it is found that the large ionisation disappears when oxygen is fed in so as to destroy the afterglow. As before, this is not a mere dilution effect, since the afterglow, and the ionisation with it, reappear when an equal stream of (inert) nitrogen is substituted for the oxygen tributary.

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* The air afterglow does not appear to give rise to any measurable ionisation, even when very conspicuously developed.

The galvanometer deflection is increased several fold if sodium vapour is introduced into the nitrogen between the testing electrodes, so as to develop the sodium spectrum.

Mercury vapour, introduced into the glowing nitrogen, did not much alter the conductivity of the latter, though its spectrum was completely replaced by the line spectrum of mercury.

Acetylene under the same conditions diminished the conductivity about three times. The cyanogen spectrum was alone visible in the region between the electrodes. For comparison of conductivities it was replaced by an equal stream of diluent nitrogen.

The chief point of interest brought out by these last experiments is that there is not always a much higher conductivity associated with the development of a line spectrum than with the development of a band spectrum. The spectra do not appear to be due to the recombination of ions. This was tested to some extent in the case of glowing nitrogen itself in the former paper.* An improved experiment has been carried out as follows: In order to make the most of the available voltage (200 volts) it was applied to a condenser with plates only 0·7 mm. apart. The glowing gas flowed between these plates along a length of 4 cm., and its luminosity could be observed by looking edgewise between them. A key was arranged so as to connect the plates together when up, and to connect them to the 200-volt supply when depressed. The luminosity was unaltered in intensity on depressing the key, whether the glow between the plates was that due to active nitrogen alone, or to acetylene or iodine stimulated by it. These spectra are therefore unaffected when a field of about 3000 volts per centimetre is applied to remove the ions.

The above condenser was not suitable to experiments with mercury vapour, as it was apt to be short-circuited by drops of condensed mercury. In this case I contented myself with passing the glow through a field of 100 volts per centimetre. No effect was observed.

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* P. 221.

5. *Development of Metallic Spectra—Analogy with Ozone.*

I have seen no reason to modify the opinion before expressed that metallic line spectra developed in the afterglow are to be regarded as due to the combustion of the metal in active nitrogen. This opinion is supported in several cases by independent evidence that nitrogen is absorbed and a compound formed.

I have succeeded in observing analogous phenomena when metallic vapours are brought into contact with ozone. A current of oxygen was passed through a vacuum tube at low pressure, and a fragment of thallium heated to perhaps 300° C. in the issuing ozone. A spontaneous combustion of thallium vapour in ozone was observed with production of green thallium light. This at once ceased when the ozonising discharge was stopped. A similar combustion was obtained with sodium vapour, showing the D line only, without the green line so conspicuous when active nitrogen is used. No spectrum was observed with mercury. These phenomena are inconspicuous compared with those given by nitrogen. They are often interfered with by oxidation of the metallic surface, which hinders free evolution of vapour. I have not been tempted to study them in more detail.

6. *Attempts at Condensation.*

All attempts to isolate the active nitrogen by liquid air condensation have failed.

A closed vacuum tube, containing pure nitrogen, was partly immersed in liquid air, and the jar discharge passed for a considerable time. The afterglow was well developed, diffusing into those portions of the tube out of the direct line of discharge. No change of pressure could be observed, such as would be expected if any condensation of active nitrogen occurred. A tube charged with oxygen quickly runs "hard" under similar conditions, owing to the condensation of ozone.

These observations seem very unfavourable to the idea that active nitrogen has a complex atomic grouping, and, as far as they go, favourable to the idea before suggested, that it is monatomic. The simplicity of its spectrum in the visual region as compared with the ordinary nitrogen spectrum may be thought to point in the same direction.

7. *Summary.*

(1) Oxygen destroys active nitrogen, but does not combine with it. Hydrogen has no action.

(2) Active nitrogen, in reacting with nitric oxide to form the peroxide,

gives the same greenish-yellow flame with continuous spectrum which may be obtained by stimulating oxides of nitrogen in other ways.

(3) The reaction just mentioned is used to determine the percentage of active nitrogen present in ordinary nitrogen as it leaves the discharge. The result found is about 2·5 per cent., much higher than was formerly supposed.

(4) When dilute phosphorus vapour is introduced into glowing nitrogen it does not react at once. It is not until some time after the glow has completely disappeared that the nitrogen gets into a state in which it can react with phosphorus.

(5) The glow has a large electrical conductivity, comparable with that of a salted Bunsen flame. The ions are liberated in the glow, not merely carried forward from the original discharge. This ionisation is, as a rule, not very greatly affected when the spectra of other substances, such as metals or cyanogen, are developed by the active nitrogen in the space between the testing electrodes.

(6) None of these spectra are visibly diminished in intensity when large electromotive forces are applied to remove the ions.

(7) Ozone can in some cases develop metallic spectra when mixed at comparatively low temperatures with the metallic vapour.

Analysis of Tidal Records for Brisbane for the Year 1908.

By F. J. Selby, M.A.

(Communicated by Dr. R. T. Glazebrook, F.R.S. Received October 20,—
Read November 23, 1911.)

(From the National Physical Laboratory.)

The National Physical Laboratory has recently carried out an analysis of tidal records for Brisbane (lat. 27° 20′ S., long. 153° 10′ E.) for the year 1908, and in view of the importance of all such figures to those investigating tidal theory it has been thought desirable to publish the results.

The records analysed are for the complete year 1908, obtained from a recording tide gauge at the Pile Lighthouse in Moreton Bay on the outer edge of the bar of Brisbane River, and were furnished by Mr. E. A. Cullen, Engineer to the Harbours and Rivers Department, Brisbane. The scale is 1·644 inches to the foot. Mr. Cullen states that "as the effect of freshwater discharge of the river is absolutely negligible, save during the somewhat rare floods, the data may be considered as observed at an open coast station." He further remarks on the regularity of the tides, and states, with reference to previous predictions, in which eight harmonic components have been employed, that an error of more than 3 inches in height is unusual.

In the records as furnished a smooth curve had been drawn over the pencil trace obtained from the tide gauge, greatly facilitating the work of measuring the heights, and the actual trace was, in general, no longer visible. It is necessary to remark that in several instances errors had been made in drawing the smooth curve; as is usual, a number of days were recorded on one sheet, and the draughtsman sometimes passed from the trace for one day to that for the succeeding day, 24 hours later. It is believed, however, that all such errors have been detected and the correct interpretation adopted.

The method of analysis employed is that due to Sir G. H. Darwin and explained in the paper "On an Apparatus for Facilitating the Reduction of Tidal Observations."* Sir G. H. Darwin's tidal abacus as there described was used, with the guide sheets and computation forms prepared by him. These, however, do not include forms for the tides 2 N, MN, MK, 2 MK. These tides are included on the India Office tide-predicting machine at the National Physical Laboratory, and hence, though they are of no great importance, it was thought worth while to analyse for them. Guide sheets and computation forms for these four components were accordingly prepared.

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* 'Roy. Soc. Proc.,' 1892, vol. 52, pp. 345—389; 'Scientific Papers,' vol. 1, pp. 216—257.

Sir G. H. Darwin's computation forms include some components which are not represented on the tide-predicter. In the table of the harmonic constants appended (Table I) these components are given in the second column to distinguish them from the 24 components included on the machine and used in the predictions.

The values of H and κ for the various components are given in Table I. The notation is that usually employed, as given by Sir G. H. Darwin in the paper referred to above, and in the British Association Report for 1883 of the Committee for the Harmonic Analysis of Tidal Observations.*

A curve was run off on the tide-predicter for the year 1908 for comparison with the observations analysed. The agreement of the actual and predicted curves appeared to be approximately of the same order of accuracy as that usually obtained in the Indian predictions, and the result was therefore considered satisfactory.

Table I.—Harmonic Analysis of Tidal Records for Brisbane for the Year 1908. Values of H and κ.

	H.	κ.		H.	κ.
	feet.	°		feet.	°
M_2	2·224	290·5	M_1	·008	138·8
M_4	·049	147·9	M_3	·024	330·1
M_6	·042	186·9			
S_1	·043	101·1	S_4	·002	182·7
S_2	·618	308·8	S_6	·002	45·6
S_a	·331	12·5			
S_{sa}	·028	326·7	R	·011	177·7
O	·390	143·3			
K_1	·695	173·8	MS_f	·008	157·7
K_2	·176	298 8	M_f	·042	256·1
P	·208	173·5	M_m	·061	187·1
N	·417	281·0			
L	·117	302·0			
ν	·117	304·1			
T	·022	308·3			
μ	·093	3·6			
J	·042	213·2			
Q	·086	124·8			
MS	·068	256·3			
2SM	·022	190·2			
2N	·090	285·6			
MN	·024	132·7			
MK	·021	7·0			
2MK	·033	233·2			

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* See Sir G. H. Darwin, 'Scientific Papers,' vol. 1, p. 5.

Height of mean sea level for the year 1908 above datum = 3·383 feet. The datum employed is the mean height of low water of spring tides.

It is desirable to compare the above results with those for other Australian ports. Sydney is the nearest port for which data are available, and is situated on the same line of coast. The data for Sydney and for some other Australian ports are given in Rollin A. Harris' 'Manual of Tides,' Part IVA, and in the tide tables for 1912 issued by the United States Coast and Geodetic Survey, and for Fremantle in Sir G. Darwin's collection in the 'Roy. Soc. Proc.,' vol. 39, 1885. The values given for Sydney are somewhat different in the first two publications; it is, however, not clear that they refer to analyses of different periods, since the record corresponding to the second set of values was available when Part IVA of Rollin Harris' Manual was published. They are derived from one year's observations of high and low waters (1888).

The principal quantities necessary for comparison of the results for Brisbane and Sydney are given in Table II. Both sets of values for Sydney are reproduced:—

Table II.

	Lat.	Long.	S_2/M_2.	N_2/M_2.	O_1/K_1.	P_1/K_1.	$S_2^\circ - M_2^\circ$.	$M_2^\circ - N_2^\circ$.	$K_1^\circ - O_1^\circ$.
Brisbane ……	27° 20′ S.	153° 10′ E.	0·28	0·19	0·56	0·30	18·3	9·5	30·5
Sydney, Fort Denison …	33° 51′ S.	151° 15′ E.	0·26 0·23	0·19 0·20	0·60 0·80	0·34 0·33	21 14	5 4	21 43

It will be seen that the agreement is close. The age of the tide for Brisbane = 18·3° ÷ 1·016° = 18 hours. This differs considerably from the mean value of 36 hours given by Sir G. H. Darwin* (the value for Bombay is 33 hours), but agrees well with the value for Sydney. The agreement as regards the age of the parallactic inequality and of the diurnal inequality is also sufficiently close.

The ratio S_2/M_2 for Brisbane is below the theoretical value, but K_2/S_2 and P_1/K_1 are in accordance with theory. The diurnal tides are "inverted."

My thanks are due to Mr. W. H. Brookes, who carried out the greater part of the computations and also checked the final reductions. The Laboratory is also indebted to the Brisbane authorities for permission to publish the results of the analysis.

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* 'Encyclo. Brit.,' 11th Edition, article "Tide."

The Distillation of Binary Mixtures of Metals in Vacuo. Part I.—*Isolation of a Compound of Magnesium and Zinc.*

By Arthur John Berry, B.A., Downing College, Cambridge.

(Communicated by C. T. Heycock, F.R.S. Received October 24,—Read November 23, 1911.)

A product of the formula AuCd has been isolated by Heycock and Neville* by placing a known quantity of gold, together with a considerable excess of cadmium, in a hard glass tube exhausted by a mercury pump, and distilling the mixture for five or six hours at a temperature as high as the glass was capable of withstanding. The composition of the non-volatile residue always approximated closely to that required by the formula AuCd, and the authors concluded that the product was a definite inter-metallic compound. It would appear, however, from the work of Vogel,† that these two metals are capable of forming the compounds Au_4Cd_3 and $AuCd_3$. The compound Au_4Cd_3 forms a series of solid solutions with cadmium, and this author concludes that the product AuCd isolated by Heycock and Neville "dürfte daher als ein kadmium-reicherer Mischkristall der Verbindung Au_4Cd_3 aus der Reihe Bc, seine Zusammensetzung als eine zufällige zu betrachten sein."‡

At the suggestion of Mr. Heycock, the author has commenced a general investigation of the distillation of binary mixtures of metals, one of which at least is readily volatile, in order to ascertain if this method is of general applicability as a means of isolating inter-metallic compounds.

It would appear *a priori* that the success or failure of such a method will depend upon two factors. Firstly, the dissociation pressure of the inter-metallic compound must be practically nil at the temperature at which the distillation is effected; and, secondly, the partial pressure of the vapour of the more volatile constituent must fall suddenly at the composition of the alloy corresponding to the formula of the compound.

Heycock and Neville§ found that, in order to ensure success in the isolation of the product of minimum vapour pressure, it was necessary to exhaust the tube very thoroughly. This circumstance is probably due to the fact that it is only in fairly high vacua that the viscosity of the residual gas is sufficiently reduced to enable the heavy metallic vapour to diffuse away from the heated part of the tube at a moderate velocity.

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* 'Trans. Chem. Soc.,' 1892, vol. 61, p. 914.

† 'Zeitsch. anorg. Chem.,' 1906, vol. 48, p. 333.

‡ *Loc. cit.*, p. 341.

§ *Loc. cit.*

The fact that the "volatilisation point" of a number of metals is greatly reduced at very low pressures appears to have been first observed by Demarçay.[*] More recently Krafft[†] has investigated the phenomena of vaporisation and boiling of metals in a cathode-ray vacuum. Krafft and Bergfeld[‡] have determined the lowest temperatures at which volatilisation of metals in a cathode-ray vacuum just takes place, and have substantially verified Demarçay's observations, especially as regards the volatility of cadmium and zinc.

Experimental.

Grube,[§] as the result of an investigation of the freezing-point curve of mixtures of magnesium and zinc, has demonstrated the existence of a definite compound of the formula $MgZn_2$. This compound is further characterised by the fact that it does not form solid solutions with either of its constituents.

With the object of isolating the compound $MgZn_2$ by distillation from an alloy containing excess of the more volatile metal, the following procedure was adopted. The magnesium together with an excess of zinc was placed in a Jena glass tube closed at one end, and bent near the middle at a very obtuse angle as in Heycock and Neville's experiments.[||] The open end of the tube was constricted to facilitate sealing off, and connected by a T-piece to a bulb of cocoanut charcoal, and to a good water pump.[¶] The whole apparatus was constructed of Jena glass. During the preliminary exhaustion by the water pump, the apparatus was thoroughly heated. The connection with the water pump was then sealed off and the charcoal cooled by liquid air. After about half an hour the tube was sealed off. The tube was then transferred to a horizontal furnace and arranged in such a manner as to allow the distillate to condense and separate from the residual alloy. The tube was heated for six or seven hours, and the zinc in the residual alloy determined volumetrically by potassium ferrocyanide solution, uranyl acetate being employed as indicator.

An experimental difficulty which was encountered in the present work was the reducing action of magnesium on the siliceous matter of the glass. The distillation was conducted at a relatively low temperature, but it was found that the glass was attacked even at temperatures below the melting point of magnesium, the interior surface becoming coated with a black deposit. This deposit was shown to consist, in part at any rate, of magnesium silicide, since it was found to be soluble in dilute hydrochloric acid with evolution of the spontaneously inflammable silicon hydride. The residual ingot was invariably contaminated with silicon, but this element was not determined quantitatively. The percentage of zinc in the product, which was found to agree with that calculated for the formula $MgZn_2$, was considered to be a sufficient criterion that the isolation of the inter-metallic compound had been effected.

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[*] 'Comptes Rendus,' 1882, vol. 95, p. 183.

[†] 'Deutsch. Chem. Ges. Berichte,' 1903, vol. 36, p. 1690.

[‡] *Ibid.*, 1905, vol. 38, p. 254.

[§] 'Zeitsch. anorg. Chem.,' 1906, vol. 49, p. 77.

[||] *Loc. cit.*

[¶] With the exception of one experiment (described below), in which the tube was exhausted by a Töpler pump, all the experiments were carried out in the manner described above, viz., preliminary exhaustion by the water pump and subsequent exhaustion by charcoal cooled in liquid air.

Results.

(1) A mixture of 1·42 grm. of magnesium and 14 grm. of zinc was sealed up in a tube. In this particular experiment the tube was exhausted by the Töpler pump. After distillation of the mixture for several hours two portions of the residue were taken for analysis, with the following results :—

(*a*) 1·433 grm. of the alloy were dissolved in hydrochloric acid and the liquid diluted to 200 c.c. 20 c.c. of this solution required 17·1 c.c. of standard potassium ferrocyanide solution (1 c.c. of $K_4Fe(CN)_6$ = 0·00696 grm. of zinc). Found Zn = 83·0 per cent.

(*b*) 0·797 grm. of the alloy was dissolved in hydrochloric acid and the liquid diluted to 100 c.c. 20 c.c. of this solution required 19·4 c.c. of standard $K_4Fe(CN)_6$ solution. Found Zn = 84·9 per cent. $MgZn_2$ requires Zn = 84·5 per cent.

(2) A mixture of magnesium and zinc in equivalent proportions, *i.e.*, 1 atom of magnesium and 2 atoms of zinc, was sealed up in a tube exhausted by cold charcoal, and distilled for several hours. A small quantity of zinc was volatilised and a little magnesium interacted with the glass. Three portions of the residue were taken for determination of the zinc-content, with the following results :—

(*a*) 0·731 grm. of the residue was dissolved in hydrochloric acid and the liquid diluted to 100 c.c. 20 c.c. of this solution required 17·8 c.c. of standard $K_4Fe(CN)_6$ solution (1 c.c. of standard $K_4Fe(CN)_6$ = 0·007 grm. of zinc). Found Zn = 85·2 per cent.

(*b*) 1·0944 grm. of the alloy was dissolved in hydrochloric acid and the liquid diluted to 100 c.c. 20 c.c. of this solution required 26·3 c.c. of standard $K_4Fe(CN)_6$ solution. Found Zn = 84·1 per cent.

(*c*) 0·6546 grm. of the alloy was dissolved in hydrochloric acid, and the liquid diluted to 100 c.c. 20 c.c. of this solution required 15·8 c.c. of standard $K_4Fe(CN)_6$ solution. Found Zn = 84·6 per cent.

We may conclude, therefore, that the alloy of minimum vapour pressure is the definite compound $MgZn_2$, which is quite stable under the conditions so far investigated.

(3) In one particular experiment in which a mixture of magnesium with an excess of zinc was distilled it was observed that a highly crystalline mass was deposited on the part of the tube which had been uppermost in the furnace at a short distance from the heated end. On analysis it was found that the zinc content was 84·9 per cent. The excess of zinc was condensed near the cold end of the tube, as in other experiments. It thus appeared probable that distillation of the inter-metallic compound from the lower (hotter) to the upper (colder) part of the tube had taken place. The fact that the excess of zinc had separated to a greater distance is doubtless due to its greater volatility, and also to the relatively low density of its monatomic molecule. The fact that the compound $MgZn_2$ can be distilled without decomposition was proved in the following manner:—

(4) The residue from experiment (2), weighing 11 grm., was sealed up in a tube exhausted by cold charcoal. A piece of loosely fitting iron pipe was employed to surround the part of the tube exposed to the heat of the furnace, with the object of heating the upper part of the tube to approximately the same temperature as the lower. Distillation was allowed to proceed for between five and six hours. At the end of this time practically the whole of the alloy had condensed just beyond the heated part of the tube, a small quantity of zinc had volatilised to a greater distance, and the interior of the heated part of the tube was, as usual, coated with magnesium silicide. The temperature at which this particular distillation was carried out was somewhat higher than in other experiments, inasmuch as the glass collapsed to a slight extent. The distillate was analysed by titration of the zinc with sodium sulphide solution, sodium nitroprusside being employed as an external indicator.

In this work it was found that in some cases the end-point in titrating zinc by potassium ferrocyanide was obscured by the appearance of a bluish colour in the liquid. Possibly a trace of iron may have found its way into the alloy from the glass in which the reaction mixture was heated. No such difficulty occurred when the zinc was titrated with sodium sulphide, the end-point with sodium nitroprusside being quite satisfactory.

Analysis of the Distillate.

(*a*) 1·893 grm. of the distillate were dissolved in hydrochloric acid and the liquid diluted to 200 c.c. 20 c.c. of this solution required 32·35 c.c. of sodium sulphide (1 c.c. = 0·005 grm. Zn). Found Zn = 85·2 per cent.

(*b*) 1·5735 grm. of the distillate were dissolved in hydrochloric acid and the liquid diluted to 200 c.c. 20 c.c. of this solution required 26·7 c.c. of sodium sulphide. Found Zn = 84·8 per cent.

The conclusion is therefore inevitable that the compound has been distilled unchanged. It is true that the compound has not been obtained in a perfectly pure condition, being invariably contaminated with traces of silicon, but this in no way invalidates the conclusion arrived at. This constitutes, so far as the present writer is aware, the first recorded example of an inter-metallic compound which has been distilled without decomposition.

Experiments on other pairs of metals will doubtless lead to results of interest. The number of pairs of metals, one of which at least is readily volatile, which are capable of giving rise to a single compound only is, however, very small. The most numerous series are those of varying degrees of complexity in which a number of inter-metallic compounds are formed. In many cases, too, the systems are complicated with the formation of solid solutions. Various refinements will probably be required in the experimental methods, and, in particular, it is intended to conduct the distillations in an electric furnace, with a view to regulating the temperature as accurately as possible.

The author desires to express his cordial thanks to Mr. Heycock for the great interest he has taken in these experiments and for his valuable suggestions.

On the Conductivity of a Gas, between Parallel Plate Electrodes, when the Current Approaches the Maximum Value.

By JOHN S. TOWNSEND, F.R.S., Wykeham Professor of Physics, Oxford.

(Received November 2,—Read November 23, 1911.)

The relation connecting the current with the potential difference between parallel plate electrodes when the gas between the plates has been uniformly ionised by Röntgen rays or Becquerel rays has been investigated theoretically by many physicists. In all cases various assumptions are made in order to simplify the calculations, as the problem becomes very complicated when the disturbance of the field due to the separation of the ions is taken into consideration.

Perhaps the most complete solution is that given by Mie,* in which the only effect that is neglected is that of diffusion. The difference between the velocities of the positive and negative ions is taken into consideration, and the disturbance of the field due to the charge in the gas produced by the excess of ions of one sign in the neighbourhood of the electrodes. The method of analysis, consisting of a series of approximations, is difficult, but the results have been presented in a convenient form, for currents in air at atmospheric pressure that are certain fractions of the saturation current. A curve is given for each current which shows the distribution of force between the plates. The currents investigated ranged between those that were one-fifth and nine-tenths of the saturation current. In the former case the ratio of the electric force at the negative electrode to the minimum force in the field was found to be 2·7. The ratio diminishes as the force increases, and for the current that is nine-tenths of the saturation current the ratio becomes 1·39.

Another investigation of the field of force between parallel plate electrodes when a current is flowing is given by Sir J. J. Thomson,† in which equal velocities are attributed to positive and negative ions. The conclusion arrived at is that the ratio of the maximum to the minimum force is 2·51, a constant quantity, independent of the current or of the intensity of ionisation. The number 2·51 corresponds to air at atmospheric pressure. For lower pressures the ratio is said to increase and to vary inversely as the square root of the pressure. These conclusions are unsatisfactory, as it can easily be shown that the ratio of the maximum to the minimum force is not constant but diminishes as the rate of ionisation is reduced, or as the force increases. Also for a given force and intensity of ionisation the polarisation of the gas must diminish as the pressure is reduced.

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* Mie, 'Ann. der Physik,' 1904, vol. 13, p. 857.

† 'Conduction of Electricity through Gases,' pp. 84—87.

The method adopted by Mie is necessarily very complicated, as it applies to cases in which there are large variations in the field of force, and as it is necessary for many purposes to know the degree of saturation corresponding to a given electromotive force the following simple investigation of the conductivity of a gas between parallel plates when high forces are used may be of interest.

It is easy to see that when the potential difference between the electrodes is sufficiently large the polarisation may be neglected and the field of force between parallel plates may be considered uniform. The conductivity in a uniform field is therefore of a kind that can be realised in practice, and from the solution of the equations obtained for that case it can be shown how the charge in the gas increases as the force is reduced, and it is possible to find exactly the percentage by which the current falls below the maximum current before the field of force is disturbed to such an extent as to introduce a serious error in the determination of the current.

In order to find an upper limit to the difference between the maximum force X_1 to the minimum force X_2 in a conducting gas, it is necessary to find the charge in the gas between the two points at which the forces are acting. Let ν_1 and ν_2 be the numbers of positive and negative ions per cubic centimetre when the steady state is reached and a current i is flowing. If e denotes the charge on an ion the current i per unit area of the electrodes is $e(\nu_1 u_1 + \nu_2 u_2)$ where u_1 and u_2 are the velocities of the positive and negative ions. Letting $n_1 = e\nu_1$ and $n_2 = e\nu_2$, then

$$i = n_1 u_1 + n_2 u_2.$$

The velocities of the ions are proportional to the electric force, so that

$$u_1 = k_1 X \quad \text{and} \quad u_2 = k_2 X.$$

Also let a be the distance between the electrodes. The difference between the greatest and smallest force is

$$X_1 - X_2 = 4\pi \int (n_1 - n_2)\, dx = 4\pi \int \left[\frac{n_1 u_1 + n_2 u_2}{u_1} - \frac{n_2(u_1 + u_2)}{u_1} \right] dx.$$

Hence
$$X_1 - X_2 < 4\pi \int \frac{i}{u_1}\, dx,$$

where the integral is taken over the distance between the two points at which the forces are acting, which is less than the distance a.

Hence, if u_1' is the least velocity in the field,

$$X_1 - X_2 < \frac{4\pi a i}{u_1'}, \quad \text{so that} \quad \frac{X_1 - X_2}{X_2} < \frac{4\pi a i}{k_1 X_2^2}.$$

The force X_2 may be increased to a large value, but the current i remains constant when the saturation point is reached, and the quantity $(X_1 - X_2)/X_2$ becomes so small that the force may be considered constant.

Let the space between the plates be ionised uniformly by rays producing q/e positive or negative ions per cubic centimetre in unit time, and let the rate of recombination be αe, so that the number of ions of either kind that recombine per second is $\alpha e \nu_1 \nu_2$.

When the steady state is reached the rate at which ions are being generated per unit volume must be equal to the loss by recombination, together with the loss by the outward motion of ions through the boundary of the volume. When the diffusion of the ions is neglected the steady state is represented by the equation

$$\frac{q}{e} = \alpha e \nu_1 \nu_2 + \frac{d}{dx}(\nu_1 u_1),$$

or

$$\frac{d}{dx}(n_1 u_1) = q - \alpha n_1 n_2. \tag{1}$$

Similarly

$$-\frac{d}{dx}(n_2 u_2) = q - \alpha n_1 n_2. \tag{2}$$

Eliminating n_2 from the above equation, the following differential equation for $n_1 u_1$ is obtained :—

$$\frac{d}{dx}\left\{\frac{u_2}{\alpha n_1}\left(q - \frac{d}{dx}(n_1 u_1)\right)\right\} = -\frac{d}{dx}(n_1 u_1),$$

which on integration gives

$$\frac{d}{dx}(n_1 u_1) = \frac{\alpha}{u_1 u_2}\left[n_1^2 u_1^2 + C n_1 u_1 + q\frac{u_1 u_2}{\alpha}\right].$$

The constant of integration C is equal to $-i$, where $i = n_1 u_1 + n_2 u_2$ is the current per unit area between the plates.

On integration this equation gives

$$\frac{1}{\sqrt{(q u_1 u_2/\alpha - \frac{1}{4} i^2)}} \tan^{-1}\left(\frac{n_1 u_1 - \frac{1}{2} i}{\sqrt{(q u_1 u_2/\alpha - \frac{1}{4} i^2)}}\right) = \frac{\alpha x}{u_1 u_2} + C_1,$$

or

$$n_1 u_1 - \tfrac{1}{2} i = \sqrt{(q u_1 u_2/\alpha - \tfrac{1}{4} i^2)} \tan\left(\frac{\alpha}{u_1 u_2}(x - \tfrac{1}{2} a)\sqrt{(q u_1 u_2/\alpha - \tfrac{1}{4} i^2)}\right), \tag{3}$$

the constant C_1 being determined by the conditions $n_1 u_1 = i$ when $x = a$, and

$n_1 u_1 = 0$ when $x = 0$. The equation (4) connecting the current i and the electric force X is also obtained from the latter condition

$$\sqrt{\left(\frac{4qk_1k_2\mathrm{X}^2}{\alpha i^2}-1\right)}\tan\left[\frac{\alpha a i}{4k_1k_2\mathrm{X}^2}\sqrt{\left(\frac{4qk_1k_2\mathrm{X}^2}{\alpha i^2}-1\right)}\right] = 1. \tag{4}$$

In order to see over what range of forces this equation may be considered to hold accurately, it is necessary to find to what extent the field becomes disturbed by the charge $n_1 - n_2$ per cubic centimetre of the gas. For this purpose it will be sufficient to consider that the ions move with equal velocities, so that there will be the same increase of force at each electrode, and the minimum force will be at the centre of the field.

Let $p^2 = 4qk_1k_2\mathrm{X}^2/\alpha i^2$, then equation (3) becomes, on substituting for i its equivalent $n_1u_1 + n_2u_2$,

$$n_1u_1 - n_2u_2 = i\sqrt{(p^2-1)}\tan\left\{\frac{2q}{i}\,\frac{x-\frac{1}{2}a}{p^2}\sqrt{(p^2-1)}\right\},$$

in which u_1 and u_2 may be taken as equal, and a mean value of the difference between the forces at the electrodes X_1 and the minimum force X_2 will be given by the equation

$$\mathrm{X}_1 - \mathrm{X}_2 = 4\pi\int_0^{a/2}(n_1-n_2)\,dx = -\frac{4\pi i^2 p^2}{2qu}\log\cos\left\{\frac{aq}{i}\,\frac{\sqrt{(p^2-1)}}{p^2}\right\},$$

or

$$\frac{\mathrm{X}_1-\mathrm{X}_2}{\mathrm{X}} = -\frac{8\pi k_1k_2}{\alpha k}\log\cos\left\{\frac{aq}{i}\,\frac{\sqrt{(p^2-1)}}{p^2}\right\}. \tag{5}$$

where k is the mean velocity of an ion under unit electric force.

As an example of the application of equations (4) and (5) the conductivity of air at atmospheric pressure may be considered. In this case the mean velocity of the ions may be taken as 450 cm. per second under a force of one electrostatic unit, and $\alpha = 3400$, so that equation (5) becomes

$$\frac{\mathrm{X}_1-\mathrm{X}_2}{\mathrm{X}} = -3{\cdot}3\log\cos\phi, \tag{5a}$$

where

$$\phi = \frac{aq}{i}\,\frac{\sqrt{(p^2-1)}}{p^2}. \tag{6}$$

Since the investigation applies only to cases in which the ratio $(\mathrm{X}_1-\mathrm{X}_2)/\mathrm{X}$ is small, equation (5) *a* shows that ϕ must be a small angle, so that from equation (4), which reduces to $p^2-1 = \phi^{-2}-\frac{2}{3}$, equation (6) gives

$$\frac{i}{aq} = \frac{1}{1+\frac{2}{3}\phi^2}. \tag{6a}$$

This shows that the current must be nearly saturated, since aq is the maximum value of i.

The current in terms of the electric force is given by the equation

$$\frac{4qk_1k_2X^2}{ai^2} = \frac{1}{\phi^2}+1 = \frac{1}{\phi^2}, \tag{7}$$

since ϕ is a small quantity.

On substituting the values of the constants for air at atmospheric pressure the following relation is obtained:—

$$X = \frac{\sqrt{(ai)}}{15{\cdot}5} \times \frac{1}{\phi}. \tag{7a}$$

This equation, combined with the equations

$$\frac{i}{aq} = \frac{1}{1+\frac{2}{3}\phi^2}, \quad \text{and} \quad \frac{X_1-X_2}{X} = \frac{3{\cdot}3\,\phi^2}{2},$$

gives the corresponding variables in terms of the parameter ϕ. Thus, giving ϕ the values 0·1, 0·141, and 0·3, the following relations hold for air at atmospheric pressure:—

$\phi = 0{\cdot}1$ .... $X = \frac{\sqrt{(ai)}}{1{\cdot}55}$; $i = \frac{aq}{1{\cdot}006}$; $\frac{X_1-X_2}{X} = 0{\cdot}016$,

$\phi = 0{\cdot}141$ ...... $X = \frac{\sqrt{(ai)}}{2{\cdot}17}$; $i = \frac{aq}{1{\cdot}012}$; $\frac{X_1-X_2}{X} = 0{\cdot}033$,

$\phi = 0{\cdot}3$ .... $X = \frac{\sqrt{(ai)}}{4{\cdot}65}$; $i = \frac{aq}{1{\cdot}06}$; $\frac{X_1-X_2}{X} = 0{\cdot}148$.

The first row of figures show that in order to get a current that is 0·6 per cent. less than the maximum the mean electric force is given by the equation $X = \sqrt{(ai)}/1{\cdot}55$, and that there is a variation of 1·6 per cent. in the electric force in the field between the plates. Thus if the distance between the plates a be 1 cm. and the current $q = 10^{-3}$ in electrostatic units the potential difference between the plates is 6·1 volts.

In order to see to what extent the method is accurate, when applied to currents several per cent. less than the maximum current, the figures in the third row may be considered. In that case the force at the electrodes is greater by 15 per cent. than the force at a point midway between the plates where the rate of recombination is greatest, since the product n_1n_2 has a maximum value in that region. The length of time the ions are in the gas, where they recombine most rapidly, is therefore about 7 per cent. longer than that allowed for, and the numbers of positive and negative ions present are also greater than the computed numbers by the same percentage, owing to the reduction in the velocity of the ions. Consequently, the amount of recombination is underestimated to the extent of about 14 per cent., so that the current i should be $aq/1{\cdot}07$ instead of $aq/1{\cdot}06$.

The effect of reducing the pressure may be found by substituting for the numerical constants their values for low pressures. The velocities k_1 and k_2 vary inversely as the pressure, and according to the most reliable determinations of the variation of the rate of recombination with pressure, which have been made by Langevin, the quantity α varies approximately in direct proportion to the pressure. If the pressure be reduced to the nth part of an atmosphere the equations for determining the variable quantities become

$$X = \frac{\sqrt{(\alpha i)}}{15{\cdot}5} \times \frac{1}{n^{3/2}\phi}; \quad \frac{i}{\alpha q} = \frac{1}{1 + \frac{3}{5}\phi^2}; \quad \frac{X_1 - X_2}{X} = \frac{3{\cdot}3 n^2 \phi^2}{2}.$$

So that for a pressure of 1/100th atmosphere, when the current and electric force are the same as at one atmosphere, these equations give, on substituting for ϕ the value 10^{-4},

$$X = \frac{\sqrt{(\alpha i)}}{1{\cdot}55}; \quad \frac{i}{\alpha q} = \frac{1}{1 + 6 \times 10^{-9}}; \quad \frac{X_1 - X_2}{X} = 0{\cdot}00016.$$

So that the effect of polarisation is reduced to 1/100th part of its original value, and the current practically attains its saturation value. In practice, however, the current would not be so easily saturated, for the effect of diffusion increases as the pressure is reduced in the same proportion as the velocities of the ions, and at low pressures the effect of recombination in reducing the current is generally of less importance than the effect of diffusion, which causes some of the ions to be lost by coming into contact with the electrode opposite to that towards which they tend to move by the action of the electric force.

On the Iron Flame Spectrum and those of Sun-spots and Lower-type Stars.

By Sir NORMAN LOCKYER, K.C.B., F.R.S.

(Received November 2,—Read November 23, 1911.)

In 1897 I announced to the Royal Society* that the lines in the spectra of the metallic elements might be separated into two series, one seen best and sometimes alone in the hotter stars, and when higher temperature and electric energy were employed, these I termed "enhanced lines"; the other set, not visible in the hotter stars, but in stars of the solar type, and seen best with lower degrees of heat and electric energy in the laboratory, were referred to as "arc lines."

In a previous paper, published in 1904,† I pointed out that the similarity of spot spectra and that of Arcturus depended upon the equality in temperature of the vapours existing in these celestial light sources. At this time it was held by Prof. Hale and his colleagues, who had studied and published‡ in detail the lines in the spectra of lower-type stars, that the occurrence of spot lines in these spectra indicated the presence on such stars of many spots like those on the sun. In a later publication, however, they state§ that their recent work has led them to the opinion that the comparatively low temperature of these stars offers the simplest explanation of the observations.

It followed naturally that the enhanced lines, representing a higher degree of temperature, or greater electrical excitement, which I showed‖ exist almost alone in some of the high temperature stars, such as α Cygni, should, in the spectra of sun-spots and lower-type stars, be weakened. That this is so has been noted by Fowler¶ and by Mitchell.**

It seemed important to consider as a third term the spectrum given by the comparatively low temperature of the oxy-hydrogen flame and see how the lines in this spectrum behave in the spectra of sun-spots and lower-type stars.

In connection with some researches on meteorite spectra in 1887, many photographs of oxy-coal-gas flame spectra—iron amongst the number—were taken with low dispersion. I gave a short list of lines in the flame spectrum of iron in a paper[*] submitted to the Royal Society in that year. The wave-lengths of these lines were necessarily given only approximately, so for this present enquiry it has been considered necessary to obtain the oxy-hydrogen spectrum of iron with much greater dispersion and showing more detail. The 3-inch Cooke spectrograph has been used for this purpose, the source of heat being an oxy-hydrogen blow-pipe flame. This spectrum, the lines of which are in course of tabulation, shows many lines which do not appear to have been previously recorded in the flame spectrum. Hartley in 1894 published a record of the lines[†] occurring in the oxy-hydrogen flame spectrum of iron. A comparison of his record with that obtained from the Kensington photograph shows that many lines occurring in the latter were not recorded by Hartley, and there are numerous discrepancies in wave-length between the two sets. This is probably due to the fact that much less dispersion was used by Hartley.

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* 'Roy. Soc. Proc.,' 1897, vol. 60, p. 475.

† 'Roy. Soc. Proc.,' 1904, vol. 74, p. 53.

‡ 'The Spectra of Stars of Secchi's Fourth Type' (The Decennial Publications, Chicago University, 1903).

§ 'Ast. Phys. Journ.,' 1906, vol. 24, p. 185.

‖ 'Roy. Soc. Proc.,' 1899, vol. 64, p. 322.

¶ 'Monthly Notices,' 1906, vol. 61, p. 361.

** 'Ast. Phys. Journ.,' 1906 ,vol. 24, p. 83.

It is found that the iron flame lines which occur in the region covered by Hale's sun-spot maps are, in general, similarly affected. They show extensive winging in the spot spectrum rather than an increase in the intensity of the line in passing from Fraunhoferic to sun-spot spectrum. It has been noted by Adams,[‡] in connection with his work on the spectra of the electric arc core and flame, that the lines relatively much stronger in the flame of the arc are those most affected in sun-spots. The majority of these pronounced "flame of arc" lines exist in the oxy-hydrogen flame spectrum.

By the kindness of Dr. Glazebrook, Director of the National Physical Laboratory, I was enabled to arrange for Dr. H. A. Harker and Mr. C. P. Butler to take several photographs of the furnace spectrum of iron. For this they used one of the large electric resistance-tube furnaces which have recently been installed at the Laboratory. On comparing these with the oxy-hydrogen flame spectrum, it is found that the lines which exist at the lowest temperature of the furnace are just those which occur in the oxy-hydrogen flame. At the higher temperatures employed in the furnace, in addition to the lines just referred to, some of the lines seen in the arc appear; but here again the flame lines are relatively strong as compared with the other lines.

The behaviour of these lines in passing from the solar spectrum to that of Arcturus and α Orionis has been studied. This, however, cannot be done in the same detail as in sun-spots, on account of the very much smaller dispersion of the stellar photographs, and consequent bunching of groups of lines of which the individual components can easily be seen in the case of spot spectra. In the more refrangible part of the spectrum, roughly from λλ 4330 to 4000, the flame lines appear to be mainly unaffected in passing from the solar spectrum to that of Arcturus. In the α Orionis spectrum in the same region there is too much absorption to make a satisfactory comparison. In the region from λλ 4330 to 4500 the evidence tends to show that most of the lines are strengthened both in Arcturus and α Orionis. Owing to the difficulty previously referred to of separating the flame lines in stellar spectra from neighbouring lines possibly due to other elements, the strengthening of the flame lines in these stellar spectra cannot be definitely established until stellar photographs of much greater dispersion are available.

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[*] 'Roy. Soc. Proc.,' 1887, vol. 43, p. 120.

[†] 'Phil. Trans.,' 1894, vol. 185, p. 199.

[‡] 'Ast. Phys. Journ.,' 1909, vol. 30, p. 112.

The reduction of the lines in the flame spectrum and the comparison of the lines in the laboratory and stellar photographs has been done by Mr. F. E. Baxandall. The photograph of the flame spectrum used in this enquiry was taken by Mr. W. E. Rolston. I have already referred to Mr. Butler's part in the work.

Address of the President, Sir Archibald Geikie, K.C.B., at the Anniversary Meeting on November 30, 1911.

The first duty which devolves upon us at these Anniversaries is to take note of the losses by death which the Society has suffered during the year that has passed. The sadness which cannot but be felt in recounting these losses and realising by how much poorer they have made the Society is, perhaps, somewhat lessened on the present occasion by the fact that our ranks have suffered rather less diminution than usual. On the Home List we have lost thirteen Fellows, on the Foreign List only one.

At the Anniversary last year, in presenting the Copley Medal, I had an opportunity of briefly referring to some of the leading features in the career of SIR FRANCIS GALTON, to whom the Medal had been awarded. Within a few weeks thereafter that distinguished man, full of years and honours, passed to his rest. In the brief interval of these weeks, I had the pleasure of visiting him at his temporary home in the country, and of hearing from his own lips how greatly he was gratified that the Royal Society, of whose Fellowship he was always so appreciative, should have bestowed on him its highest honour. It was, he said, the crowning distinction of his life. I did not think at the time that it would be the last mark of recognition that would come to him, for he looked as well as he had done for a long time; his keen interest in scientific progress was unabated, and his mind and memory clear as ever. In him we mourn an accomplished and generous man of science, who devoted his long life and energies to the advancement of natural knowledge. It is a pleasing remembrance to us that in conferring the Copley Medal upon him the Royal Society brightened the last days of one of the most loyal of its Fellows.

On the side of the physical sciences the Society has lost some prominent representatives. In Dr. JOHNSTONE STONEY another has passed away of that brilliant band of physicists whom Ireland has given to science. He died on July 1 last at the ripe age of 85, carrying with him to the grave the affectionate regrets of a wide circle of friends, who appreciated his scientific labours and lifelong enthusiasm, and who esteemed his gentle and kindly nature.

SAMUEL HAWKSLEY BURBURY, who was a very regular attendant at our meetings, died on August 31, in his 80th year. He had at Cambridge a career which was remarkable for combining the highest honours in classical literature with mathematical distinction. He was called to the Bar in

1858, and, in the midst of his legal work, found time to extend his mathematical studies. He thus became a high authority on the dynamical theory of gases and other branches of physical mathematics.

JOHN BROWN, formerly a linen manufacturer, of Belfast, who only died at the beginning of the present month, deserves to be remembered as another representative of the now dwindling class of men of business, who devote their leisure to scientific pursuits and the promotion of knowledge. His papers on the seat of the electromotive force in voltaic combinations, especially on the influence of the surrounding medium, contributed substantially to the elucidation of that subject. He became a Fellow of the Society in 1902.

FREDERICK JERVIS-SMITH, formerly Millard Lecturer in Experimental Mechanics at Trinity College, Oxford, and a devoted worker in that subject, was remarkable for his skill in the construction of delicate mechanical appliances in the laboratory which he fitted up in his College. He was elected into the Society in 1894, and died on August 23 last, at the age of 63.

MERVYN HERBERT NEVIL STORY-MASKELYNE was the bearer of a name which is honoured in the history of science and in that of the Royal Society, and which received additional distinction from his own labours. For almost forty years Professor of Mineralogy at Oxford, and for twenty years of that period likewise Keeper of the Department of Minerals in the British Museum, he stood at the head of mineralogical science in this country. By his lectures, his writings, and, above all, by his labours in the augmentation and arrangement of the admirable mineral collection in our National Museum, he did much to encourage the study of mineralogy, which had been somewhat neglected in Britain.

JOHN ATTFIELD will be remembered for the value of his contributions to chemical pharmacology. By his teaching and writings, and his constant personal exertions in raising the standard of education among pharmaceutical chemists, he rendered great service to the branch of applied science which he cultivated. He died on March 18 at the age of 76.

Besides these losses on the Home List from the ranks of our physicists and chemists, we have to record, with sincere regret, the death of one of the most notable of our Foreign Members, the illustrious JACOBUS HENRICUS VAN'T HOFF. His genius, combining a remarkable union of mathematical acumen, experimental resource, and faculty for bold and lofty generalisation, opened up new domains in chemistry. His work on 'Chemistry in Space' laid the foundations of stereo-chemistry, and his 'Studies in Chemical Dynamics' placed that side of the science on a well established basis. In recent years he has been engaged on a series of elaborate researches into the conditions in which deposits from saline solutions can be formed in the sea. His papers on this subject throw fresh light on the history of accumulations of this nature which are intercalated among the strata of the earth's crust, and his work is thus of interest alike to the chemist and the geologist.

On, the side of the biological sciences, six of our Fellows have died during the past year. The cause of research in tropical medicine has suffered a grievous loss by the premature death of SIR RUBERT BOYCE. His career of only forty-eight years has been marked by unwearied energy and enthusiasm in the contest with the malignant diseases that are the scourge of man in tropical climates. Not merely did he personally carry on researches in this country and encourage others to co-operate in the same cause, but, throwing himself into the breach, he again and again sailed to the Tropics for the purpose of enquiring into the maladies on the spot. His labours, and those of the other investigators who have studied yellow fever, have been rewarded, and now that fatal malady has been successfully combated.

Of the physicians on the list of our Fellows we have to record the deaths of three eminent men. JOHN HUGHLINGS JACKSON was the founder of the modern school of neurology in this country. Perhaps his greatest work was his discovery, on purely clinical grounds, of the localisation of function in the centre of the brain—a discovery that has been verified and greatly extended by a long series of experimental researches by other observers.

FREDERICK WILLIAM PAVY, for so many years a familiar figure at our meetings, has passed away in his eighty-third year. He has held a high place among the physicians of his day, not only as an eminent practitioner, but as an accomplished and assiduous man of science, who devoted his long life mainly to one special branch of investigation—the part played by sugar in the economy of the animal system. The important bearing of his investigations on diabetes and other diseases has long been recognised both in this country and abroad.

SIR SAMUEL WILKS was remarkable for the keen insight shown in his recognition of the fact that medicine must rest on the science of pathology. He devoted his life and teaching to the development of this principle. His contributions to pathological knowledge were many and valuable in themselves, but they acquired additional importance from the correlation which he established between the findings of pathology and of morbid anatomy on the one hand, and the natural history of disease, as seen clinically, on the other. To the end of his life he took the greatest and most appreciative interest in the new and striking developments of his own favourite science.

To our late associate, Dr. JOHN BEDDOE, the science of anthropology stands greatly indebted. Born in 1826 and educated for the medical profession, he began, when only 20 years of age, to make those observations on the facial and other features of living races which, throughout his busy professional life, he continued to prosecute till he became the most learned and accomplished authority on the anthropological history of the human races of Britain and of the European Continent.

The name of THOMAS RUPERT JONES has been for nearly two generations a household word among the palæontologists and geologists of this country. Although his own more particular branch of enquiry lay among the Entomostraca and Foraminifera of past ages, on which he was the highest authority, he possessed a wide range of acquirement in all departments of geology. His ample stores of knowledge were always freely placed at the service of other workers in science. Born in 1819, he passed away last spring at the advanced age of 92.

The Report of the Council for the past year, now in the hands of the Fellows, gives a summary of the work on which the Society has been engaged since the last Anniversary. There are one or two features in this Report to which I should like to call attention. In my Address last year I adverted to the history of seismological observation in this country and to the part taken in the development of this branch of observational science by our associate Dr. Milne. I expressed the hope that means might be found to place his important service on a more permanent footing, with an enlarged staff and more generous financial aid. Though no important advance has yet been made towards the realisation of this hope, the subject has not been lost sight of, and at least one useful step has been taken in the more complete equipment of Eskdalemuir Observatory as a seismological station. There are now installed there the complete Galitzin apparatus and the twin Milne apparatus, which record photographically, and also the Wiechert and the Omori instruments, the observations of which are recorded on smoked paper. To Prof. Schuster we are indebted for his generosity in presenting the Galitzin apparatus. The various instruments, when completely put into working order, will supply valuable material for a comparison of results and will provide an important addition to the network of seismological stations in this country. The addition of this seismological work to the other duties of the Superintendent of the Eskdalemuir Observatory has shown that an increase of the staff under his supervision is imperatively required. The Gassiot Committee, after a full consideration of the subject, has recommended that a grant in aid for a limited period should be made by the Royal Society, and the Council, approving of the proposal, has granted a sum of £450 for the purpose of supplying an additional observer for two years, after which some other more permanent arrangement must be provided. In the meantime the Council has been gratified by the gift of £200 from Mr. Matthew Gray for the purpose of assisting the progress of seismology at Eskdalemuir.

Fellows are aware that for many years past the Society has been conducting researches into the cause and prophylactic treatment of tropical diseases, and that these researches are still in progress. Much information has been collected, and it is satisfactory to know that, since steps have been taken to remove the native population from the fly-belts, the areas affected by one of the most terrible of these maladies, Sleeping Sickness, have been considerably restricted. But much remains to be accomplished before the knowledge of the subject can be made as complete as it should be. As will be seen from the Report of the Council the investigation is now about to be extended far beyond the bounds originally contemplated. It has been plausibly suggested that Sleeping Sickness may be transmitted from other sources than infected human beings, and the question arises whether the wild animals of tropical Africa may possibly supply the trypanosomes of that disease. Accordingly, at the request of the Colonial Office, the Royal Society has organised and despatched a new Commission, under the directorship of Sir David Bruce, for the purpose of studying on the spot what may be the relation of the native fauna of Nyasaland and other parts of Africa to the spread of human trypanosomiasis, and what trypanosome diseases may affect the domestic animals of that region. The composition of the staff has been carefully considered with a view to secure adequate attention to each of the various branches of investigation that are embraced in the wide enquiry which is projected. It is interesting to know that Lady Bruce, who has all along been one of the most efficient observers in Africa, again accompanies her husband on this fresh expedition. I may add that she is not the only lady engaged under our auspices in Africa; Miss Robertson, who has had considerable experience in the study of trypanosomes, has volunteered her services in Uganda and is now at the Mpumu laboratory, tracking the development and transmission of the organisms to which trypanosomiasis is due.

To what is said in the Council's Report regarding the progress of the National Physical Laboratory I have one important addition to make. The Fellows of the Society who may not have previously heard will now be grieved to hear of the serious illness which last month attacked our esteemed and accomplished colleague, the Director of the Laboratory. After a time of painful suspense Dr. Glazebrook slowly began to recover, and is now happily on the high road to convalescence. But it may be some months before he can again attend to the work of the Institution over which he presides with such constant assiduity and skill.

The 'Catalogue of Scientific Literature for the Nineteenth Century,' on which the Committee of the Royal Society has now been engaged for over fifty years, is speedily approaching completion. The material for the final part (1883—1900) of the General Catalogue, which is classified under authors' names, has been collected and sorted, and is nearly ready to pass through the press. Of the subject-indexes of scientific papers for the nineteenth century, two volumes, Pure Mathematics and Mechanics, have been published; and the Index for Physics, in two volumes, is well under way. While the Committee do not claim perfection in detail for the classification of the subject-matter of those sciences, and while they are aware that the arrangement of so great a mass of material which must be condensed into small space will always be liable to technical criticism in details, they nevertheless believe that it may be confidently claimed that no person who in future shall set about a general investigation or an historical survey in any department of one of these sciences can afford to neglect consultation of this index. It was felt to be worth while by so great a man as Thomas Young, a hundred years ago, to devote a large amount of time to the compilation of a classified index of the literature of Natural Philosophy, up to that date, when the achievement was just within the range of private enterprise. The immense volume of the scientific literature of the last century could have been digested only by some corporate organisation; and the whole scientific world have signified in advance their obligation to the Committee of the Society and to the generous benefactors who have assisted the Society in the work when its own funds had been depleted, by undertaking the continuation of the same work in the twentieth century as the 'International Catalogue of Scientific Literature.'

Having gone to so much trouble and expense in the preparation of the materials for these subject-indexes, the Society is naturally desirous to see that the results become accessible to the scientific public, for whose use the volumes are intended. All the funds which the Royal Society can possibly devote to this work are necessary for its completion; thus there can be no question of free exchange, as was the case with the earlier volumes, however much the Royal Society might desire it. But, as the Fellows are already aware, the Cambridge University Press have consented to undertake the entire risk of printing and publication, and have agreed to sell the volumes at a very moderate price. We are informed that the volumes of the Index already issued have, for some reason, not yet attracted the attention among Universities and public libraries that was confidently anticipated. I have therefore thought it desirable to bring this matter to notice to-day.

On July 15 of next year the Royal Society will have lived for exactly two centuries and a-half. Looking back upon this long career, and considering the friendly relations which the Society has for generations maintained with the men of science in all quarters of the globe, the President and Council have thought that the occasion will be one which ought not to be passed over in silence, but which deserves to be marked in some worthy way. They have accordingly decided to invite the chief universities, academies, scientific societies, and other institutions in this country, in our Colonial Dominions and abroad, to send delegates hither to join with us in celebrating our 250th birthday. The invitations will be issued next month, so as to allow ample time for the selection and the arrangements of the delegates, and for our own preparations here. Our patron, His Majesty the King, has been pleased to signify his appreciation of the importance of our proposed celebration. Though the details of the function have not yet been settled, it is thought that the first reception and welcoming of our guests should be held in our own rooms, which, with their portraits and other memorials of our past, will doubtless be of interest to the visitors. For the banquet, at which the Fellows and their guests will dine together, we hope to enjoy the use of a large hall specially lent to us for the occasion. Considering the early association of the Royal Society with Gresham College and the City, we trust that some opportunity will be afforded to us of renewing that intercourse, and thus of allowing our delegates to partake of the well-known hospitality of London. There will doubtless be a good deal of private hospitality. Of course, every facility will be arranged for our guests to see public buildings, museums, libraries, and other objects of interest. At the end of the function in London, the delegates may not improbably be invited to visit the Universities of Oxford and Cambridge.

As a permanent memento of the occasion, the Council has decided to reproduce in facsimile the pages of the Charter-book, containing the signatures of the Fellows from that of the founder, Charles II, down to the present day. This interesting volume is now in course of preparation at the Oxford University Press. It has also been arranged to issue a new edition of the Society's 'Record,' in great part re-written, closely revised, and brought up to date. This volume is also in progress.

MEDALLISTS, 1911.

THE COPLEY MEDAL.

The Copley Medal is this year awarded to Sir George Howard Darwin for his long series of researches on tidal theory, including its bearing on the physical constitution of the earth and on problems of evolution in the planetary system.

As regards the actual oceanic tides, he has perfected the method of harmonic analysis initiated by Lord Kelvin, and has greatly promoted its practical application by the invention of simplified methods of ascertaining the tidal constants of a port from the observations and of framing tide-tables. In another series of researches the tides of a solid planet of slightly viscous material are investigated, including the consequent secular changes in the motion of the planet and of the tide-generating satellite. He traced from this point of view the past history of the earth and moon, and was led to the now celebrated hypothesis that the latter body originated by fission from its primary when in a molten state.

He has further studied in great detail the classical problem as to the possible figures of equilibrium of a rotating mass of liquid and their respective stabilities, which has engaged in succession the attention of Maclaurin, Jacobi, Kelvin, and Poincaré. The difficult theory of a binary system composed of two liquid masses revolving in relative equilibrium, now known as Roche's problem, has been greatly developed and extended by him. Such investigations have, of course, an important bearing on the theory of the evolution of the earth-moon system already referred to.

The above is a mere summary of the main lines of Sir George Darwin's activity. There are in addition a number of highly important memoirs on more or less cognate subjects. For example, in dealing with the question as to the degree of rigidity of the earth as it now exists, he has treated it from various points of view; he has considered the theory of the long-period tides, and the stresses produced in the interior by the weight of continents and mountain chains. The inferences of Kelvin and Darwin as to a high rigidity have, it is well known, been recently confirmed in a striking manner by the work of Hecker on the lunar disturbance of gravity. It is to be observed in this connection that Darwin's own early attempts (in conjunction with his brother Horace) to measure this lunar effect directly, though not immediately successful, have had a great influence on the subsequent history of the subject, as well as on seismometry.

Mention should also be made of remarkable papers on the history of meteoric swarms, and (in the domain of the more classical astronomy) on periodic orbits.

Sir George Darwin's 'Collected Papers' have now been published in four volumes by the Cambridge University Press. They form a monument of analytical skill and power devoted persistently through a long series of years to the elucidation of a definite series of questions of the highest interest. The difficulties of the tasks to which he has addressed himself are enormous; but, although some of the conclusions only claim as yet to be provisional and speculative, a mass of definite achievement remains which will always rank as one of the most substantial contributions to the study of cosmic evolution.

ROYAL MEDALS.

The assent of His Majesty the King has been signified to the following awards of the two Royal Medals:—

The Royal Medal on the physical side was assigned to Prof. George Chrystal, of Edinburgh University, on account of his contributions to mathematical and physical science, especially, of late years, to the study of seiches on lakes. Conspicuous in his early years as one of Clerk Maxwell's principal lieutenants, it is to him that we owe the experimental proof of the extreme precision of Ohm's law of electric conduction ('Brit. Assoc. Report,' 1876). His memoir on the differential telephone ('Trans. Roy. Soc. Edin.,' 1880) was a notable early extension of the theory and practice of Maxwell's principles as regards inductances, now become more familiar when power transmission, as well as telephonic intercourse, proceeds by use of alternating currents. His duties as a teacher of mathematics led to the 'Treatise on Algebra,' which, besides being a book of original vein, was the earliest systematic exposition in our language of the more rigorous methods demanded in recent times in algebraic analysis. But this purely mental discipline, and its continuation in various memoirs on abstract mathematics, could not wholly occupy a mind trained originally in the school of physical science. Of late years Prof. Chrystal has been engaged with great success in a most interesting subject of research, in the theory and the observation of the free persisting oscillations of level in lakes, first observed and analysed by Forel on the Lake of Geneva. By this work he has, on the one hand, added a new interest to the scenery and the physical geography of the Highlands, and, on the other hand, has extended the domain of the exact application of the principles of mathematical hydrodynamics.

At the moment when the Council was adjudicating this Medal it was unaware that the illustrious mathematician at Edinburgh was then lying on his death-bed. He had been in failing health for some time, but the latest news was more favourable. The end came, however, before he could learn that a Royal Medal had been assigned to him. In these circumstances it was felt that the award should not be cancelled, but that the Medal should be transmitted to his family as a visible token of the admiration with which the Royal Society regards his life-work. On appealing for the sanction of the Royal donor of the Medal, His Majesty was pleased to approve of our proposal, and to add an expression of his condolence: "The King trusts that you will be so good as to convey to the family the assurance of His Majesty's sincere sympathy in the terrible loss that they have sustained, through which so distinguished a career has been brought to a close." Those who had personal acquaintance with Prof. Chrystal mourn the extinction of a life full of charm and brightness.

The Royal Medal on the biological side has been awarded to William Maddock Bayliss, F.R.S. During the last twenty-five years, the part taken by Dr. Bayliss in the advancement of physiology has, perhaps, been unequalled by any other physiologist in this country. His work has ranged over a wide field. In his earlier papers dealing with the electrical phenomena associated with the excitatory state in glands and contractile tissues, he brought forward results which were, at the time, entirely novel, and have formed the basis of all subsequent investigations. His paper with Starling on the electrical phenomena of the mammalian heart was the first to give the correct form of the normal variation, as confirmed by later investigations with the string galvanometer.

Another subject which has engaged his attention at intervals during the whole of his career has been the question of the innervation of the blood vessels. In conjunction with other workers, he took a prominent part in mapping out the course of the vaso-constrictor fibres through the sympathetic system. More important is his work on vaso-dilator nerves and the part played by them in vascular reflexes. His confirmation of the earlier observations of Stricker, and his proof that the vaso-dilator impulses are carried as "antidromic" impulses in the fibres ordinarily subserving sensation, effected a revolution in our conceptions of nerve conduction, and showed that the law of Bell and Majendie, previously accepted as of universal application, did not express the whole truth, and that, in fact, a nerve fibre is normally the seat of processes which are both centripetal and centrifugal.

A third group of researches is represented by those on the innervation, intrinsic and extrinsic, of the intestines. Up to the appearance of the paper, written by him in conjunction with Starling, on the movements of the small intestine, the whole question was in the utmost confusion. For the first time these observers showed conclusively that the movements of the intestine are under the control of a local nervous system; and, even to the present time, the intestines are the only organs in higher animals which have been shown to be the seat of a local nervous system capable of carrying out co-ordinated reflexes.

A fourth group of papers deals with the mechanism of the pancreatic secretion. These researches, which by themselves would be sufficient to justify the award of the Royal Medal, were also carried out in partnership with his colleague, Prof. Starling. For many years physiologists have assumed the production of internal secretions by different organs which might influence other parts of the body. In these researches on the pancreas the first definite proof was brought forward of the production of a chemical substance in one organ, the duodenum, and its passage by the blood to another organ, the pancreas, as a result of events occurring in the duodenum. The secretion of pancreatic juice on the entry of the acid chyme into the duodenum had been previously regarded as a nervous reflex. Bayliss and Starling showed that it was a chemical reflex, *i.e.*, effected by the production of a specific chemical messenger which travelled by the blood, and not by the stimulation of nerve endings and the passage of impulses through nerves and the central nervous system. They showed, moreover, that this secretin was but a type of a whole group of substances which they designated hormones. The discovery of these hormones, and the precise definition of their nature and of the conditions of their activity, mark an important epoch in the development of our knowledge of the organs of the animal body.

The discovery of secretin afforded for the first time a convenient and easy method of obtaining pancreatic juice in large quantities. The investigation of the properties of pancreatic juice and of the activation of its chief proteolytic ferment by another ferment, enterokinase, secreted by the intestinal mucous membrane, has led Bayliss to a further series of researches on the mode of action of enzymes and on the closely related questions with regard to the nature of colloidal solutions. The value of this work has been universally recognised. The book on the nature of enzyme action in which Bayliss' researches are summarised has already appeared in German, while his most recent work on the osmotic pressure of colloids, as studied in solutions of colloidal dye-stuffs, is a model of the manner in which such investigations should be carried out.

DAVY MEDAL.

The Davy Medal is this year assigned to Prof. Henry Edward Armstrong, F.R.S., on account of his researches in organic and in general chemistry.

For many years he has been engaged, partly alone and partly in collaboration with many of his students and others, in the investigation of a number of important problems in organic chemistry. His series of memoirs on the terpenes, on the chemical and physical relationships which obtain among the isomerides of the naphthalene and the benzene series, and on physiological chemistry, have established a strong claim for recognition.

In addition to his direct scientific work, he has taken an active part in the discussion and criticism of current theories, and has put forward views on chemical change and on other subjects which have suggested fruitful lines of enquiry. Gifted with a scientific imagination, interested in the work of others, exceptionally well informed as to recent progress not only in chemistry but also in cognate sciences, he has had a stimulating effect on his fellow chemists, and has done much to bring together for their mutual benefit the workers in different fields.

HUGHES MEDAL.

The Hughes Medal has been assigned to Charles Thomson Rees Wilson, F.R.S., in recognition of the value of his contributions to our knowledge of the nuclei produced in dust-free gases, and of his investigations upon the nature and properties of ions in gases. Following up the well-known work of Aitken on dust nuclei, Mr. Wilson devised a special apparatus for producing a sudden cooling of a gas saturated with water vapour. After completely freeing the gas from dust particles he found that water was condensed on a few nuclei after an expansion of volume greater than 1·25, and that a dense cloud was formed when it exceeded 1·38. This work was in progress at the time of the discovery of X-rays. He immediately tried the effect of passing this radiation through the gas in the expansion chamber, and found that a dense cloud of fine water drops was produced for all expansions greater than 1·25. In this way he showed that the charged ions produced in gases by the X-rays became nuclei for the condensation of water at a definite supersaturation. This investigation was of great importance; for not only did it bring to light a very striking property of the gaseous ions, but it illustrated in a concrete way the process of ionisation in a gas, and the discontinuous nature of electrical charges. By this method each charged ion is rendered visible by becoming a centre of condensation of vapour. In later work he investigated the efficiency of the positive and negative ions respectively as centres of condensation; and he showed that equal numbers of ions were produced by X-rays and by the rays from radioactive substances. The effect of other agencies in producing nuclei in gases was examined in detail. The results of these experiments, which are now classical, were communicated in a series of memoirs published in the 'Philosophical Transactions.'

This condensation property of ions, discovered by Wilson, was utilised by Sir J. J. Thomson to count the number of ions present, and to determine that fundamental electrical unit, the charge carried by an ion in gases. Recently Mr. Wilson has perfected the expansion method to detect the effects of individual α- and β-particles. The path of each α- or β-particle through the gas is marked out by condensation of water upon the ions it produces, and the trails showing the paths of the particles can be photographed. He has also obtained photographs illustrating the distribution of ions due to the passage of X-rays through a gas, which show clearly the trails of the β-particles liberated from the atoms of matter. These experiments are of the greatest interest and importance, and visualise in a remarkable way the fundamental properties of these radiations.

A further study by this extraordinarily delicate method promises not only to afford a practical means of counting the α- and β-particles in a gas, but also to throw light upon some of the more important and recondite effects produced by the passage of different types of ionising radiation.

Mr. Wilson was one of the first to investigate the so-called natural ionisation of gases; he devised a simple type of electroscope for this purpose, which has come into general use, and he has constructed a tilted electroscope of great sensibility, which is now widely used for measurements of ionisation. He has also directed his attention to atmospheric electricity; he has devised an instrument for measuring accurately the current which passes from the upper atmosphere to the earth, and has determined the value of this current under different conditions.

On Sinhalese Iron and Steel of Ancient Origin.

By Sir ROBERT HADFIELD, F.R.S.

(Received October 12,—Read November 23, 1911.)

[PLATES 2—5.]

Introduction.

The use of iron has without doubt existed from a time dating back to a very early period in the world's recorded history. Owing, however, to the avidity of the oxygen present in the air for this metal, it has been most difficult to obtain *ancient* specimens of iron. We have therefore but little definite evidence regarding its early manufacture and use. It is for this reason the author thought that the present description of some interesting Sinhalese specimens of this nature which came under his notice during a recent tour in the East would be of interest to the Royal Society.

This is not the first time that the Royal Society has had presented to it papers on the subject. One hundred and sixteen years ago—to be exact, on June 11, 1795—Dr. George Pearson, a Fellow of the Royal Society, read a paper entitled "Experiments and Observations to Investigate the Nature of a Kind of Steel, Manufactured at Bombay, and there called Wootz, with Remarks on the Properties and Composition of the Different States of Iron."

It was the author's good fortune to visit the Colombo Museum and there see a large number of ancient specimens of iron and steel obtained from some of the buried cities of Ceylon, so well known to archæologists. These cities date from about 500 B.C. and had a continuous history up to about 1500 A.D.

Through the kindness of the Governor-General of Ceylon, Sir Henry McCallum, to whom grateful acknowledgment is here made, the author was accorded the privilege of having placed at his disposal a few of these interesting specimens for investigation. It is believed that the research which has now been carried out yields information not previously available on the subject of iron and steel specimens of known ancient origin; in fact, no previous publications appear to present any complete and authentic analyses accompanied by mechanical tests and photomicrographs showing the structure of such material.

Not only does the Colombo Museum contain this large number of interesting specimens of ancient tools and implements of various kinds, some 250 in number, but in another section of its exhibits are shown several swords of more modern date, bearing upon them the dates of the years 1374 and 1416 A.D., with Sinhalese legends inscribed upon them. To those interested in the metallurgy of iron and steel this collection makes special appeal as being the most complete and unique yet known.

The following is the description of the specimens sent to the author for the purpose of this research :—

1. Museum No. 138. Steel chisel from Sigiriya, of the fifth century (A.D.). Length, 10 inches.
2. Museum specimen, unnumbered. Ancient nail (pointed end broken off), 13½ inches long, probably also from Sigiriya, of the same date as the chisel, but the particulars are lost. It is, however, certainly very ancient and is typical of a certain class of implements found in the ruined cities of Ceylon.
3. Native billhook or "ketta," just as it came to hand from Dumbara, near Kandy, the headquarters of much mediæval native work.

In a fuller paper on this subject, given elsewhere, the author deals with (Section B) opinions of various authorities with regard to the so-called Iron and Bronze Ages; (Section C) remarks on the paper communicated in the year 1795 by Dr. Pearson, F.R.S., to the Royal Society, on Indian Wootz steel; (Section D) Heath and others on Indian and Sinhalese iron and steel; (Section E) Delhi and Dhar pillars in India; (Section F) remarks by MM. Osmond and Maspéro.

The present paper contains only the section dealing with the physical and chemical characters of the metal of the above specimens, and only a selection of the numerous photographic illustrations prepared.

A brief reference may be made to the interesting question of the hardness retentivity of ancient specimens of iron and steel. This subject has also been dealt with by Dr. Cecil H. Desch in his recent interesting work on "Metallography."

Dr. Desch speaks of the phases retained by quenching being commonly spoken of as metastable. He considered, however, that whilst experimental proof had not been produced, we were bound to assume that the metastable limit had been passed, and that the systems are correctly described as labile, not as metastable. Quenched specimens, therefore, tend spontaneously to assume an equilibrium condition by undergoing the transformation which was suppressed by quenching. It is uncertain how far the spontaneous change can proceed at ordinary temperatures. White tin, which is only stable above 18°, does not change into grey tin at 0° unless brought into contact with the new phase. Below 0° the change can occur spontaneously, although even at low temperatures it may fail to occur when the tin is kept for long periods. This would seem to indicate that the metastable limit for tin lies much below 0°.

Dr. Desch considers that hardened steel is undoubtedly labile at the ordinary temperature, and the presence of the stable phase is not necessary to initiate change. But there is little evidence that softening of steel takes place spontaneously unless the temperature is raised. He also states that Japanese swords of the XVth Century, when carefully preserved, are found to be as hard at the edge as if newly hardened; it would therefore seem that no appreciable return to the stable takes place in the course of several centuries at atmospheric temperatures. On the other hand, prolonged heating of hardened steel even at 100° produces an appreciable softening, and heating at 150° in a few minutes. The whole question of labile and metastable conditions in undercooled solid alloys demands fuller investigation.

The above statement by Dr. Desch is particularly interesting in regard to the present paper, because it shows that hardened material of ancient origin, when found in soft condition, may really have originally been quite hard. Thus, the edge of the ancient chisel, described in Experiment No. 2252, distinctly shows a defined structure in certain parts, differing from the other portion, apparently martensitic, as if it had once been in the hardened condition, but, by the expiration of time, had gradually assumed the condition in which it was now found, that is soft. On the other hand, this particular chisel may not have been hardened, although the microstructure, by the presence of troostite, seems to indicate that this may have once been the case.

Description of the Present Research Experiments.

Details of the various specimens, and an account of the research conducted, with the results achieved, may now be given, these experiments being carried out by the author at the Hecla Works Laboratory and Research Department.

Experiment No. 2252.—This was carried out upon the ancient Sinhalese chisel, being specimen marked No. 1 by Dr. Willey, and shown in fig. 14 (1), Plate 2. This dates back to the Vth Century. The specimen was very rough but without scale, and had an undulating surface, possibly due to unequal corrosion, and it is possible that the material was forged with rough implements of stone. The chisel was about 10 inches in length, and at the upper portion, away from the edge, about $1\frac{3}{16}$ inches square, $\frac{15}{16}$ inch by $\frac{9}{16}$ inch in the centre, tapering to a point as with modern tools.

Table I.—Composition.

C.	Si.	S.	P.	Mn.	Fe.	Specific gravity.
traces	0·12	0·003	0·28	nil	99·3	7·69

The difference represents slag and oxide.

Tensile Strength.—The Fremont shear test showed 16 tons per square inch elastic limit, 26 tons per square inch breaking load.

Shock Test.—The shock test, on un-nicked specimen, showed 17 kgrm. with 85° bend before breaking.

Hardness.—The Brinell ball test showed hardness numbers of 144 and 144 on the opposite side of the chisel. The scleroscope hardness number was 35.

The fracture was unsound, apparently owing to the existence of unsoundness or blowholes. The crystalline structure showed large sparkling crystals. The micro-structure of the specimens, shown by the photo-micrographs numbered fig. 15 (Photo 318, transverse section) and fig. 16 (Photo 318A, longitudinal section), brings out several points of interest. The transverse section shows that this chisel has been carbonised, the section showing the carbonised areas to be on two sides. The carbonisation varies on the two faces from saturation point (0·9 per cent. carbon) to about 0·2 per cent. carbon on the outside edge, and the depth of the carbonisation from the edge inwards is also shown to be variable. The presence of martensite and hardenite (fig. 15, Photo 318, carbonised area) suggests the important fact that the chisel has been quenched.

Some of the crystals give evidence of a structure probably due to impurities of phosphorus and sulphur. The longitudinal photographs of both the chisel and the nail show this structure. A further micro-section was prepared from the specimen cut from the nose of the ancient chisel. This photo-micrograph (not here reproduced) carries evidence, in the author's view, that it has been quenched, for the structure is in parts martensitic. Troostite is certainly also present, which is probably the result of tempering by the long lápse of time.

The author believes this is the first time there has been put on record evidence that the art of cementation must have been known 1500 to 2000 years ago, as shown by these specimens; probably, therefore, such knowledge would go back still further.

Experiment No. 2253.—This was carried out upon the ancient Sinhalese nail, specimen marked No. 2 by Dr. Willey, the Director of the Colombo Museum, and is shown specimen No. 2 (Plate 2, fig. 14, Photo 1471). This is probably of the same origin and age as the chisel just described. This nail is about $13\frac{1}{2}$ inches in length, and $\frac{5}{8}$ inch by $\frac{9}{16}$ inch at the point; the extreme point is missing.

Table II.—Composition.

C.	Si.	S.	P.	Mn.	Specific gravity.
traces	0·11	nil	0·32	nil	7·69

Tensile Strength.—The Fremont shear test showed 11 tons per square inch elastic limit, 21 tons per square inch breaking load.

Shock Test.—The shock test, on un-nicked specimen, 0·5 kgrm. by 1°; that is, it was very brittle.

Hardness.—The Brinell ball test showed hardness numbers of 117 and 209 on opposite sides of the nail. The scleroscope hardness number was 44. The fracture revealed a fine bright crystalline structure.

The micro-structure (see Plate 4, fig. 18, Photo 317A, and fig. 19, Photo 317B) indicates a remarkable conglomeration. Fig. 19 shows a weld running diagonally across the section, and along the edges of the weld there are carbonised areas. Another notable point is that on one side of the weld the slag shows the effect of the forging, whereas on the other side there is no such sign. The specimen is covered with slip bands, and has evidently undergone severe hammering, probably in its use as a nail. The carbon in the carbonised areas exists as granular pearlite; Photo 317 (not reproduced) is a transverse section, and figs. 18 and 19 are longitudinal sections, but of different fields.

The longitudinal photographs of both the chisel and the nail, figs. 16, 18, and 19, show evidence of a structure.

The fragment from the nail was heated and forged well up to about 1150° C. As forged, the Brinell ball hardness number was 120. The same material heated to 1050° C. and quenched in water showed 130 Brinell ball hardness number, showing that it was not hardened by quenching.

Experiment No. 2254.—This was carried out upon the ancient Sinhalese billhook, specimen marked No. 3 by Dr. Willey, and shown in fig. 14 (3) (Photo 1471) on Plate 2. The specimen was very rusty, being covered with a thick brown rust. The billhook is about 12½ inches in length, 3⅛ inches in width at the blade, the handle being 4½ inches in length.

Table III.—Composition.

C.	Si.	S.	P.	Mn.	Specific gravity.
traces	0·26	0·022	0·34	traces	7·50

Tensile Strength.—The Fremont shear test showed 16 tons per square inch elastic limit, 29 tons per square inch breaking load.

Shock Test.—The shock test on un-nicked specimen gave 7·1 kgrm. by 35° bend only.

Hardness.—The Brinell ball test showed hardness numbers of 153 and 166 on opposite sides of the billhook. The scleroscope hardness gave number 23.

The fracture showed bright crystalline structure, laminated appearance.

The report on the micro-structure of the specimen, as shown by photomicrographs, figs. 20 (Photo 319) and 21 (Photo 319A) on Plate 5, is that the specimen contains a large amount of slag, and appears to represent what would be now termed a somewhat low quality of wrought iron, There seems to be practically no carbon present, and therefore no evidence of treatment other than forging can be obtained. Fig. 20 is the transverse section and fig. 21 the longitudinal section.

Special interest attaches to the analyses given, as they probably represent the only modern complete and accurate determination of the composition of known and authentic specimens of ancient iron.

The percentage of phosphorus is, it will be noted, high, from 0·28 up to 0·34 per cent., which, however, does not greatly differ from modern bar iron. The sulphur percentage is extremely low, showing that a very pure fuel, no doubt charcoal, was employed in the production of the material. There is very little silicon present and manganese is entirely absent, which is somewhat remarkable, as nearly all iron contains some manganese.

As the specimens from which to produce ordinary tensile pieces were too small, tests were obtained by means of the ingenious Fremont shear-test method. The tensile quality of the material averages about 26 tons per square inch, or a little higher than wrought iron. This, no doubt, is owing to the considerable percentage of phosphorus present, which stiffens or hardens iron. The Fremont shock tests show fair results on the specimen taken from the chisel, namely, 17 kgrm. with 85° bend. The other specimens, however, show much lower figures, namely, the nail, 1 kgrm. by only 1° bend, and the billhook 7 kgrm. by 35° bend. The hardness by the Brinell method varied from 117 to 166, one result from the nail showing 209, but this is abnormal and cannot be accepted as representative. The scleroscope tests varied from 25 to 44, and as a comparison it may be mentioned that dead hard steel, by this latter method, shows 100, and ordinary wrought iron about 20.

From the microscopical examination, and from the other tests carried out, the specimens represent a material of the type known as wrought iron, and not steel. The specimens somewhat resemble the material known as puddled iron, and appear to have been made from somewhat impure ore. The material is very low in its percentage of carbon, and, excepting phosphorus, also other impurities. There is present, in a lumpy irregular form, quite a large amount of slag, indicating that the material has not been submitted to anything like the amount of squeezing and forging that the modern wrought iron undergoes.

DESCRIPTION OF PLATES.

PLATE 2 (fig. 14).

(1) Ancient chisel from Sigiriya, 5th century (A.D.). Two-thirds actual size.
(2) Ancient nail, from Sigiriya, 5th century (A.D.). Two-thirds actual size.
(3) Ancient "ketta" or billhook. Two-thirds actual size.

PLATE 3 (figs. 15, 16).

Transverse and longitudinal sections of chisel, as marked. Magnification 80.

PLATE 4 (figs. 18, 19).

Transverse and longitudinal sections of nail, the longitudinal showing weld. Magnification 80.

PLATE 5 (figs. 20, 21).

Transverse and longitudinal sections of billhook. Magnification 80.

Note on the Monatomicity of Neon, Krypton, and Xenon.

By Sir WILLIAM RAMSAY, K.C.B., F.R.S.

(Received November 13,—Read November 23, 1911.)

The monatomicity of neon, krypton, and xenon has been taken for granted on somewhat insufficient evidence. When the memoir on Argon and its companions* was written it was stated that no experiments with the pure gases had been carried out on the ratio between the specific heat at constant volume and constant pressure, but that measurements made with impure samples indicated the ratio 1·67; and it was remarked that such a ratio could not have been found had any considerable portion of the mixture consisted of a polyatomic gas.

Having now at my disposal relatively large quantities of pure neon, which had served Mr. Watson, and of pure krypton and pure xenon, which had served Prof. Moore, for determining the densities of these gases, it appeared advisable to fill the gaps in our knowledge of their specific heat ratios.

The apparatus was similar to the one described in the memoir on Argon†; the wave-length of sound in neon was compared by Kundt's method with that in air; and the krypton and xenon, previously frozen and purified by pumping them free of any possible content of air, were also investigated in the same manner.

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* 'Phil. Trans.,' A, 1901, vol. 197, pp. 82 and 83.

† 'Phil. Trans.,' A, 1895, vol. 186, Part I, p. 228.

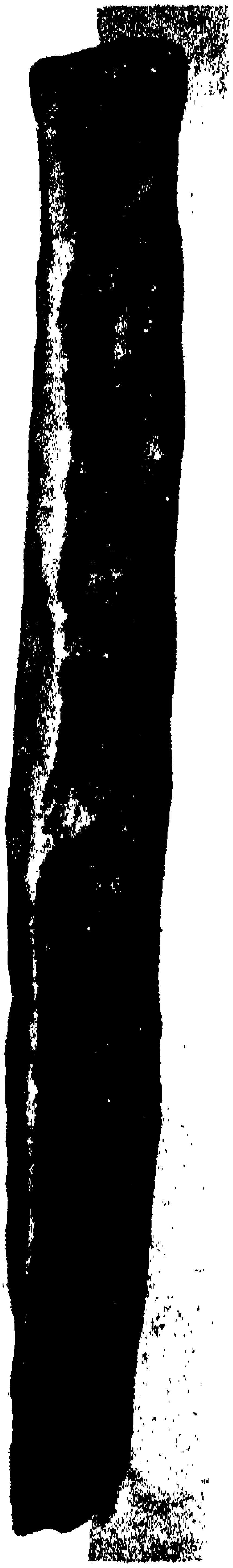


Fig 14 1

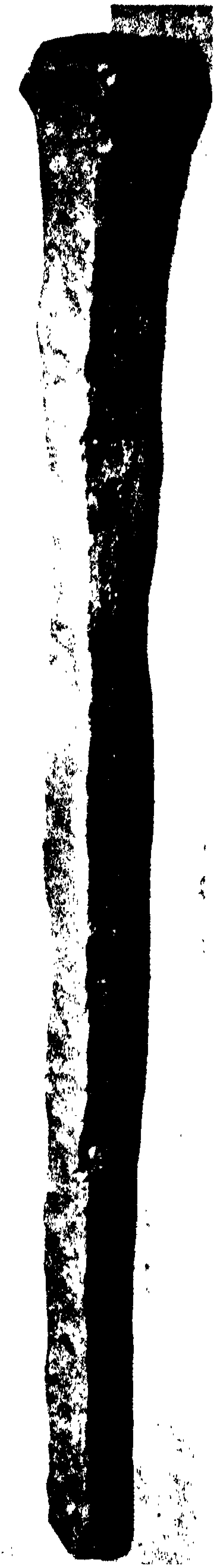


Fig 14 2

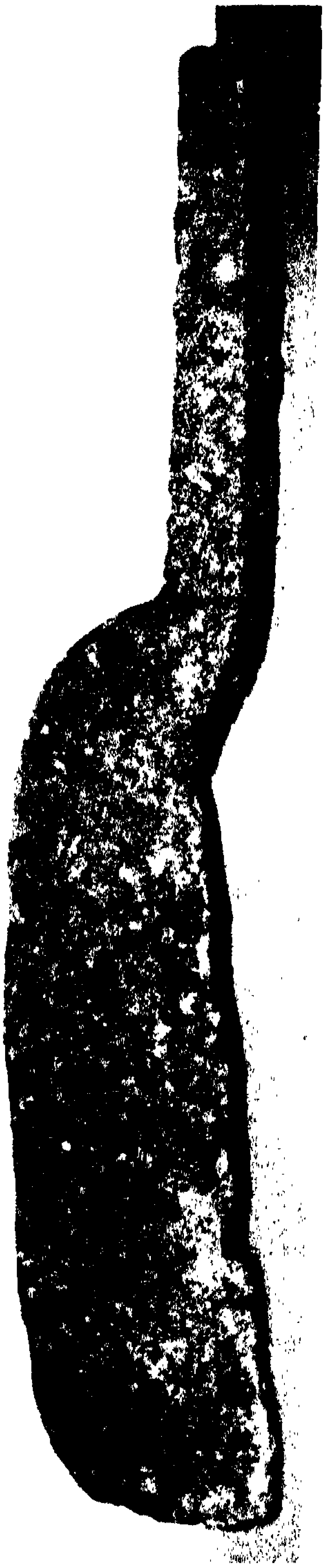


Fig 14 3

Fig. 15.

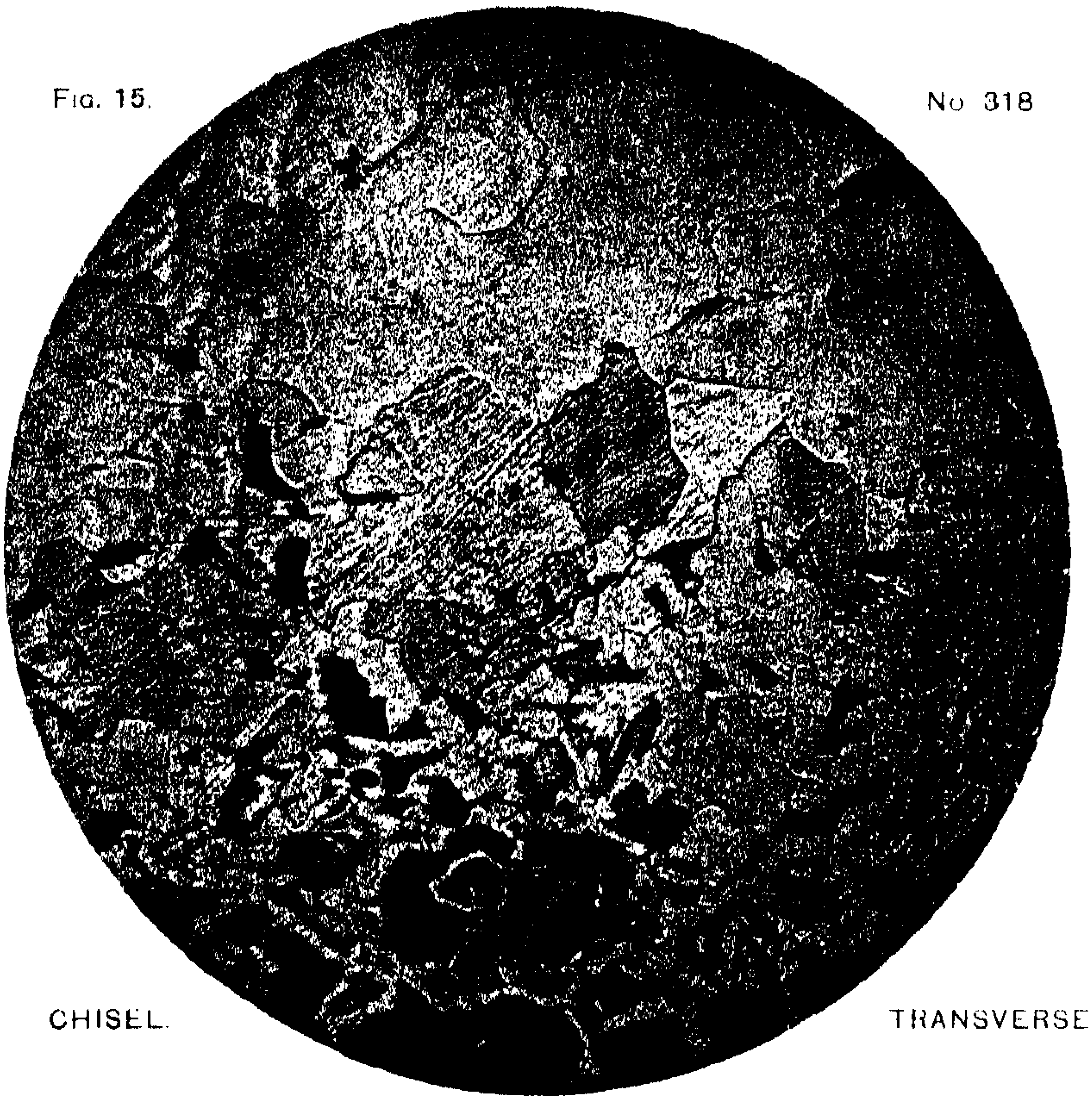


Fig. 16.

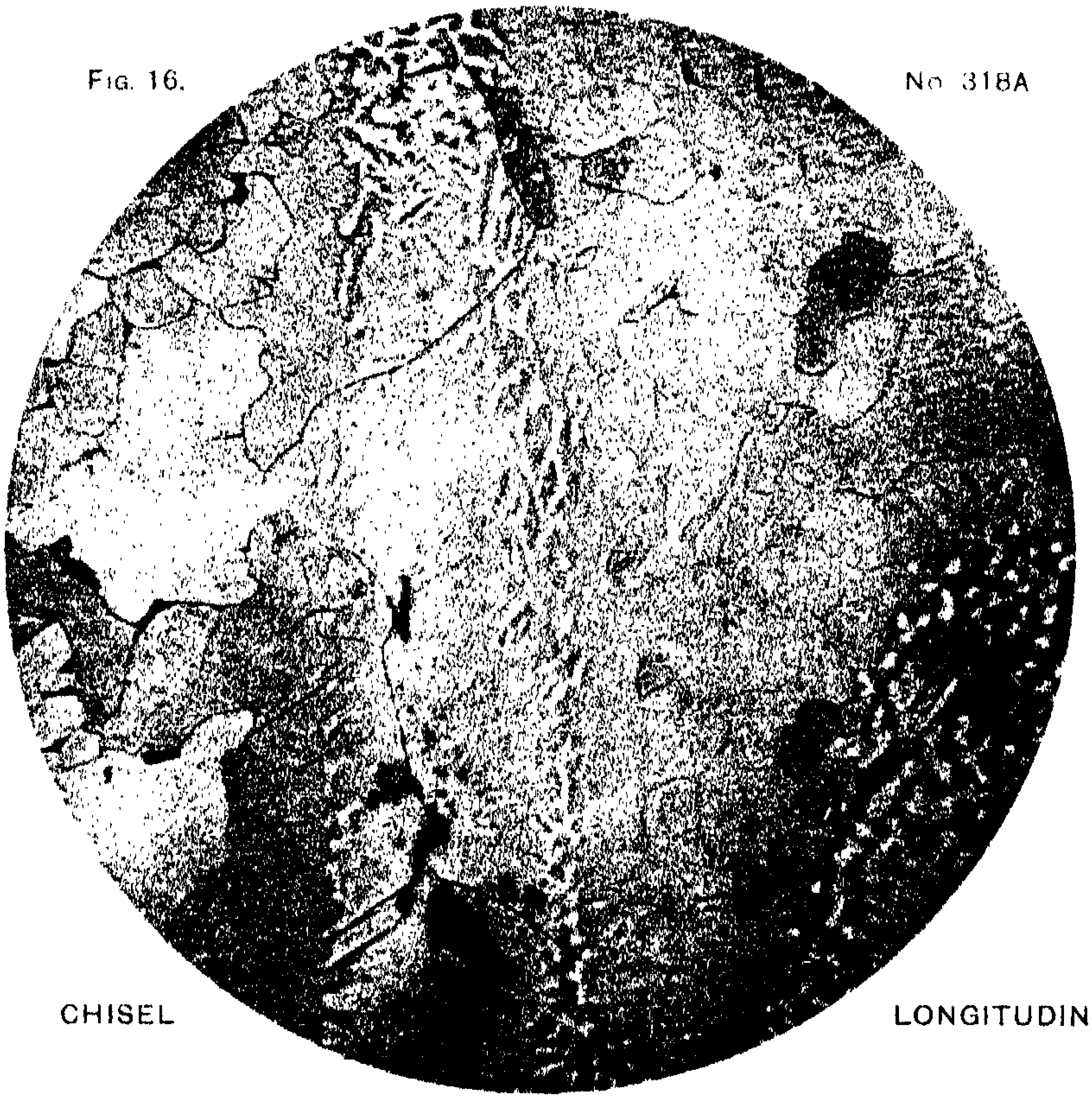
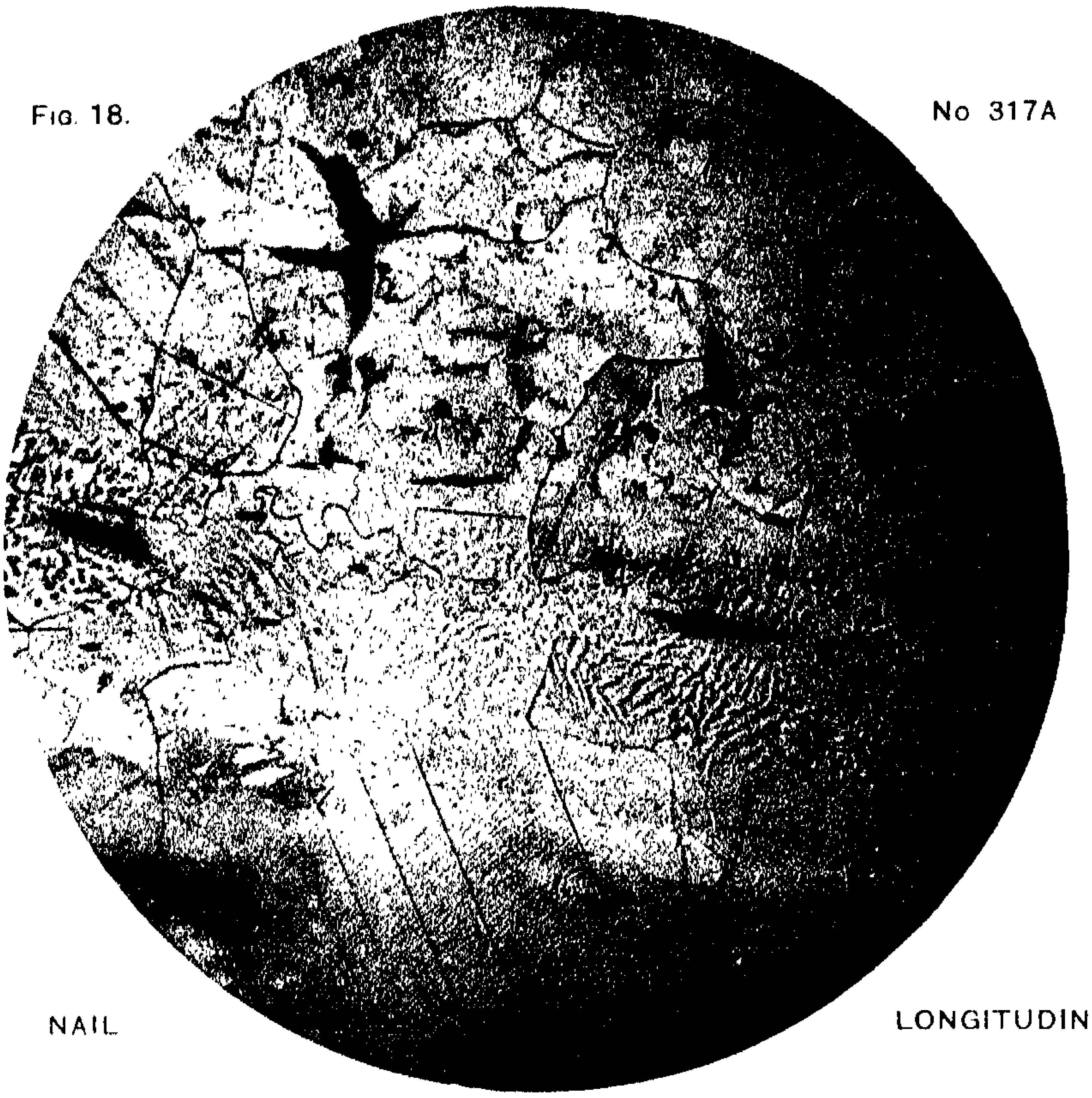
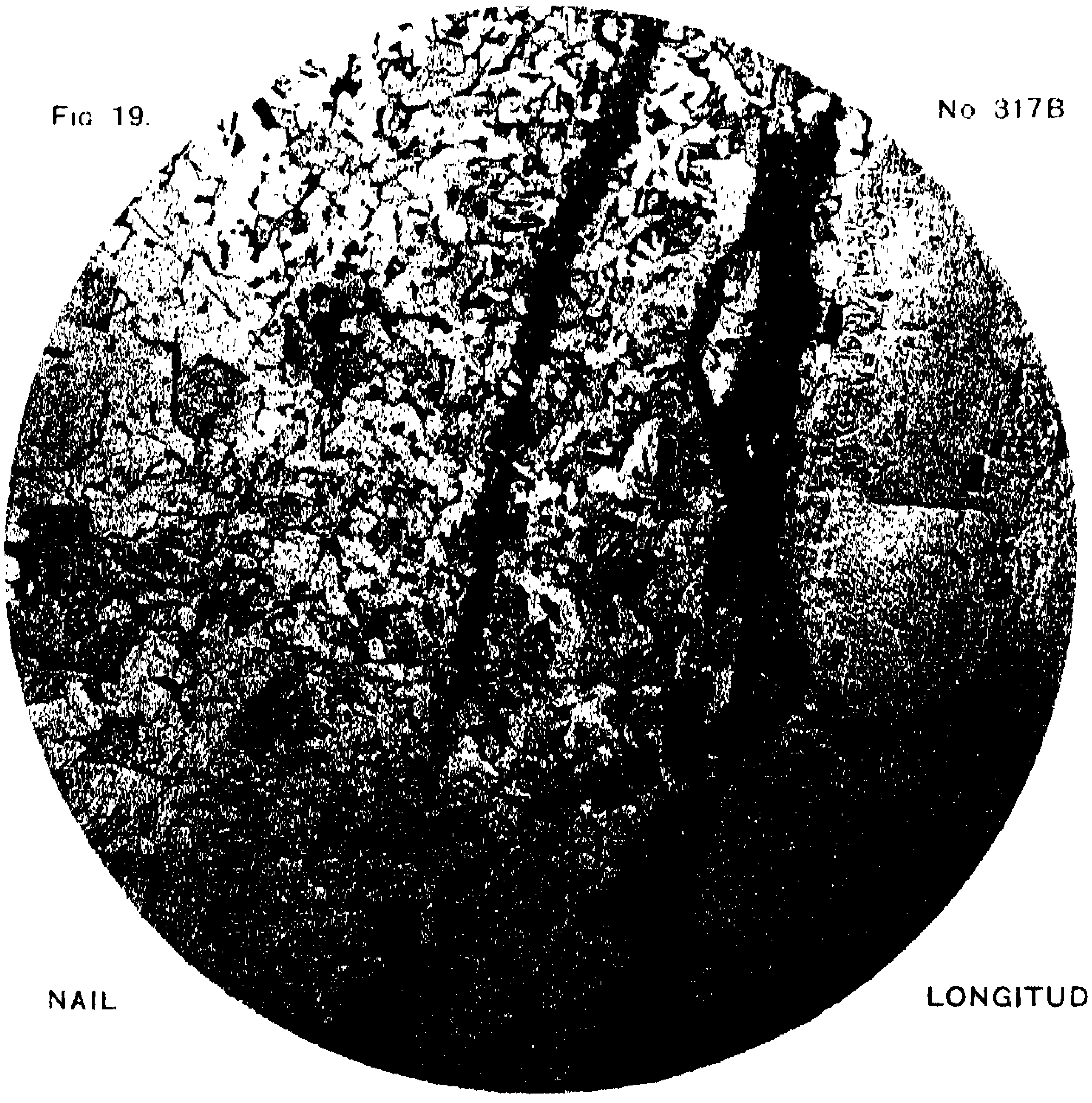


Fig. 18. No 317A



NAIL LONGITUDINAL.

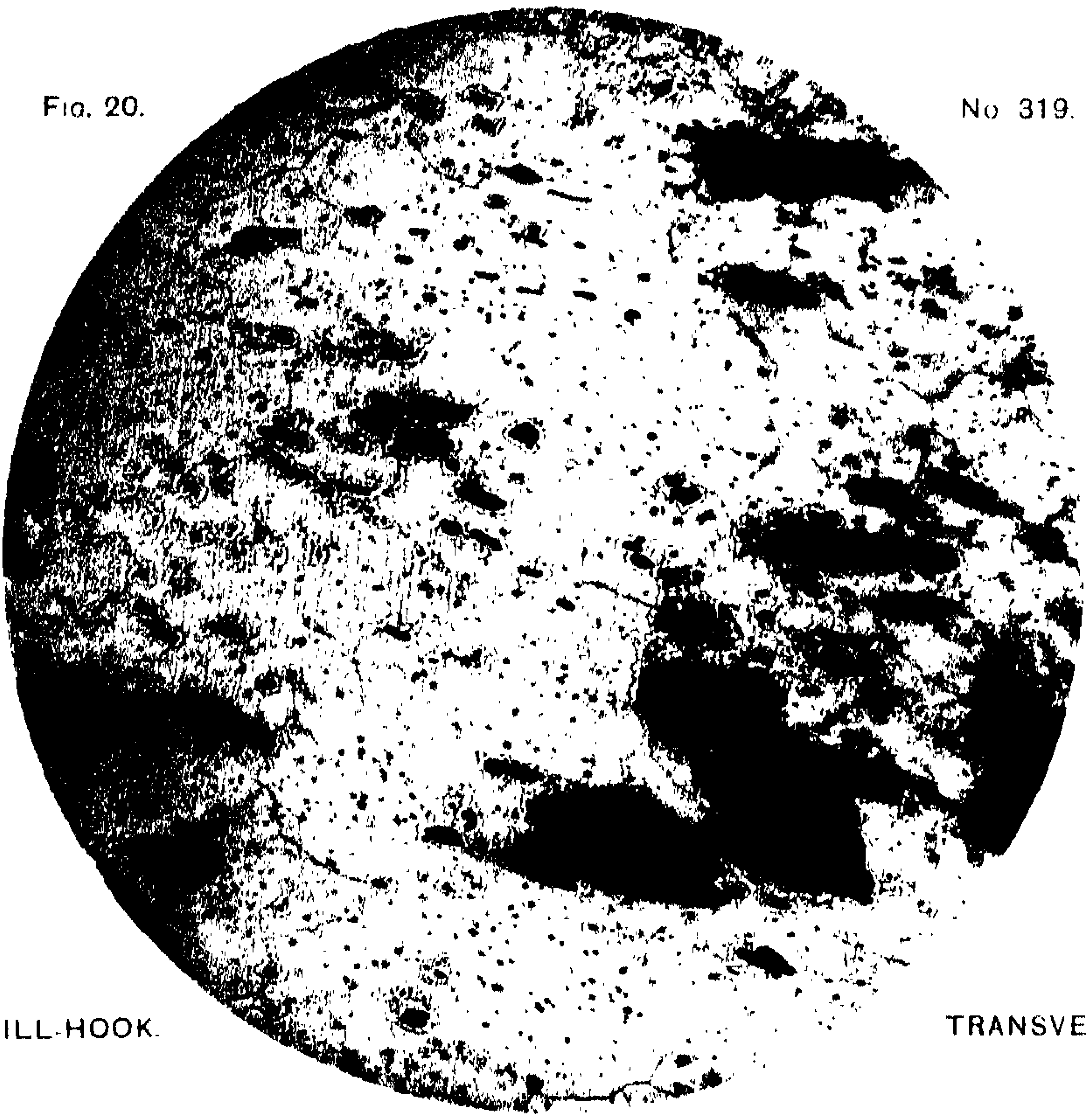
Fig. 19. No 317B



NAIL LONGITUDINAL.

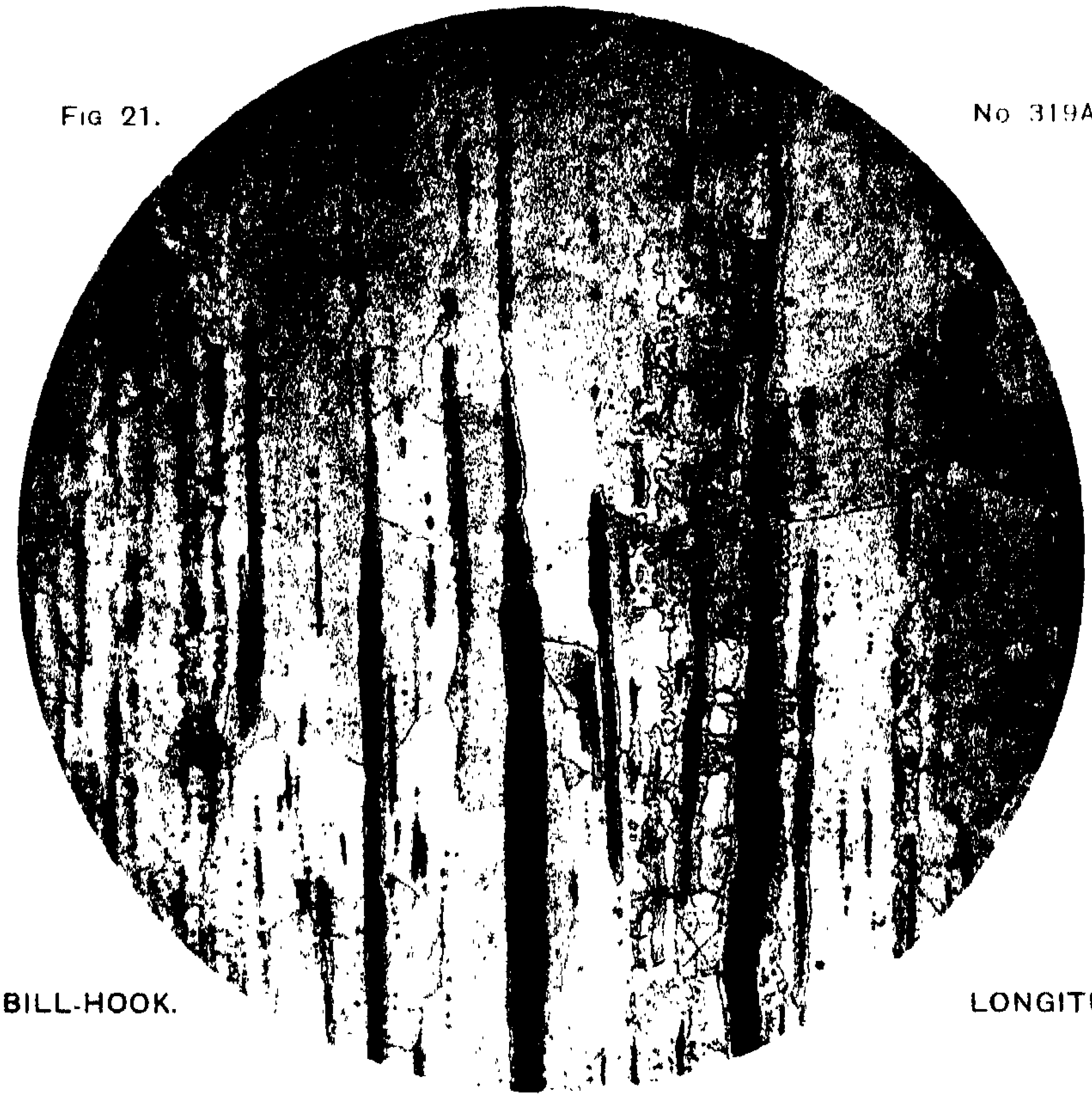
MAGNIFICATION 80.

Fig. 20. No 319.



BILL-HOOK. TRANSVERSE.

Fig 21. No 319A.



BILL-HOOK. LONGITUDINAL.

MAGNIFICATION 80.

The following results were obtained :—

				mm.
Air	at 19° C.,	half wave-length...	28·0, 27·8, 27·9, 28·1, 27·8;	mean, 27·92
Neon	„ 19·4°	„ „ ...	36·4, 35·9, 36·1, 36·1, 36·0;	„ 36·10
Krypton	„ 19°	„ „ ...	18·1, 18·2, 18·2, 18·1, 18·1,	„ 18·13
Xenon	„ 19°	„ „ ...	14·5, 14·3, 14·3, 14·3, 14·2;	„ 14·32

The formula is

$$\frac{(\text{W.L. air})^2 \times \text{density of air} \times 1{\cdot}408}{\text{Temp. abs. of air}} = \frac{(\text{W.L. gas})^2 \times \text{density of gas} \times \gamma}{\text{Temp. abs. of gas}}.$$

(Density of air, 14·479; of neon, 10·10; of krypton, 41·46; of xenon, 65·11.)

The ratios calculated from the above figures are

γ for neon	1·642
γ for krypton	1·689
γ for xenon	1·666

These numbers approximate within the limits of experimental error to the theoretical ratio 1·667, and it therefore follows that neon, krypton, and xenon, like helium and argon, must be regarded as monatomic. Their molecular and their atomic weights are identical.

The Mechanics of the Water Molecule.

By R. A. Houstoun, M.A., Ph.D., D.Sc., Lecturer in Physical Optics in the University of Glasgow.

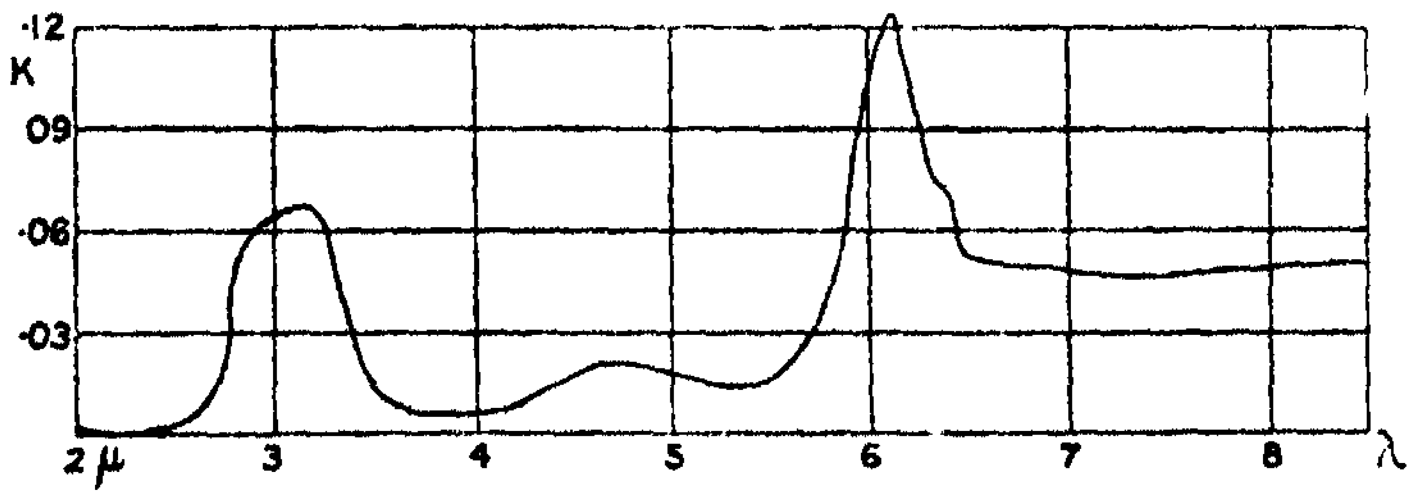
(Communicated by Prof. A. Gray, F.R.S. Received November 6, 1911,—Read January 11, 1912.)

In the ultra-violet and visible spectrum water is very transparent. In the infra-red it absorbs very strongly. E Aschkinass* has investigated its absorption in the infra-red, and has represented his results in tables, giving a constant ϵ in terms of λ, ϵ being defined by the equation

$$I = I_0 e^{-\epsilon d},$$

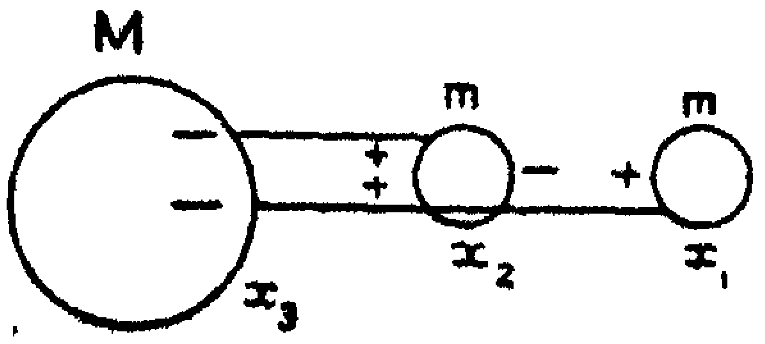
where I_0 and I are the intensities before and after traversing a layer d cm. thick. I have calculated ϵ into the more useful constant κ, $(\nu-\iota\kappa)^2$ being the dielectric constant, and have plotted the result in the following curve. The two constants ϵ and κ are connected by the relation

$$\epsilon\lambda = 4\pi\kappa.$$



ABSORPTION SPECTRUM OF WATER

From the curve it is evident that water has two great maxima at $3{\cdot}07\ \mu$ and $6{\cdot}15\ \mu$ respectively.† These occur also in water vapour; they do not occur in oxygen or hydrogen. It seems therefore plausible to connect them with the linkings of the oxygen and hydrogen atoms. A system of three atoms should, of course, have two periods.



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* 'Ann. d. Phys.,' 1895, vol. 55, p. 401.

† According to W. W. Coblentz water becomes more opaque again in the region between $8\ \mu$ and $14\ \mu$; while, according to Rubens and Aschkinass, water vapour is relatively transparent in this region.

Let the figure represent an oxygen atom of mass M and two hydrogen atoms each of mass m. The first hydrogen atom has lost one electron to the second, and the second has lost two electrons to the oxygen atom. We cannot connect the two hydrogen atoms directly to the oxygen atom, since from chemical considerations they are not situated in the same way with regard to the latter. Let x_1, x_2, x_3 be respectively the x co-ordinates of the three atoms, N the number of water molecules per cubic centimetre, and X the x component of the electric intensity in the light wave. Then, by the theory of dispersion,

$$(\nu-i\kappa)^2 = 1+4\pi \mathrm{N}e\,(x_1+x_2-2x_3)/\mathrm{X}.$$

If we write r for e/m, the right-hand side becomes

$$1+\tfrac{2}{9}\pi r\,(x_1+x_2-2x_3)/\mathrm{X},$$

since $18\mathrm{N}m = 1$. Substitute ξ_1 for x_1-x_2, ξ_2 for x_2-x_3, and the equation finally becomes

$$(\nu-i\kappa)^2 = 1+\tfrac{2}{9}\pi r\,(\xi_1+2\xi_2)/\mathrm{X}. \tag{1}$$

Now consider the equations of motion of the three atoms. Since all equations in optics are linear, the forces between the atoms must be linear functions of the distances. We can look upon the inverse-square-law pull as balanced by the structure of the atoms, or, better still, we can regard the three lines of force as acting like three equally strong spiral springs, a line of force being probably a more fundamental thing than the inverse square law. If we suppose that there is no friction, the equations of motion are then

$$mx_1''+k\,(x_1-x_2) = e\mathrm{X},$$
$$mx_2''+2k\,(x_2-x_3)+k\,(x_2-x_1) = e\mathrm{X},$$
$$\mathrm{M}x_3''+2k\,(x_3-x_2) = -2e\mathrm{X}.$$

Combine the first and second and the second and third of these equations, write $k = cm$ and $\mathrm{M} = 16\,m$, and we obtain

$$\xi_1''+2c\xi_1-2c\xi_2 = 0, \tag{2}$$

$$\xi_2''+\tfrac{17}{8}c\xi_2-c\xi_1 = \tfrac{9}{8}r\mathrm{X}. \tag{3}$$

Let the transmitted radiation be of type $e^{i\theta t}$, assume that the vibrations are forced, solve (2) and (3) and substitute in (1). Then we obtain, omitting the intermediate steps,

$$(\nu-i\kappa)^2 = 1+\frac{\pi r^2}{2}\left(\frac{0{\cdot}170}{3{\cdot}477c-\theta^2}+\frac{0{\cdot}830}{0{\cdot}647c-\theta^2}\right). \tag{4}$$

Now write $a+ib\theta$ for c in (4). This is equivalent to writing equations (2) and (3) in the form

$$\xi_1''+2a\xi_1-2a\xi_2+2b\xi_1'-2b\xi_2' = 0,$$
$$\xi_2''+\tfrac{17}{8}a\xi_2-a\xi_1+\tfrac{17}{8}b\xi_2'-b\xi_1' = \tfrac{9}{8}\,r\mathrm{X},$$

i.e., to the introduction of dissipative forces of a special kind. On equating the imaginary parts of each side, (4) then gives

$$2\nu\kappa = \frac{\pi r^2}{2}\left(\frac{0{\cdot}170 \times 3{\cdot}477\,b\theta}{(3{\cdot}477\,a-\theta^2)^2+(3{\cdot}477\,b\theta)^2}+\frac{0{\cdot}830 \times 0{\cdot}647\,b\theta}{(0{\cdot}647\,a-\theta^2)^2-(0{\cdot}647\,b\theta)^2}\right).$$

It can easily be shown that in passing through an absorption band the maximum change in ν is equal to half the maximum value of κ, and hence (*cf.* curve) must be less than 0·07. Assume that ν has the constant value 1·3 throughout the range of absorption. Then

$$\kappa = r^2\left(\frac{0{\cdot}103 \times 3{\cdot}477\,b\theta}{(3{\cdot}477\,a-\theta^2)^2+(3{\cdot}477\,b\theta)^2}+\frac{0{\cdot}500 \times 0{\cdot}647\,b\theta}{(0{\cdot}647\,a-\theta^2)^2+(0{\cdot}647\,b\theta)^2}\right).$$

The positions of the two absorption bands are given by $\theta_0{}^2 = 3{\cdot}477a$ and $\theta_0{}^2 = 0{\cdot}647a$. The ratio of their wave-lengths is therefore

$$(3{\cdot}477/0{\cdot}647)^{\frac{1}{2}} = 2{\cdot}32.$$

The actual value should be 2·00.

Let $\bar{\kappa}$ be the maximum value of κ for an absorption band, λ_0 the wave-length of $\bar{\kappa}$, λ_1 the wave-length for which κ has half its maximum value, and θ_1 the corresponding value of θ. We have respectively for the first and second bands $\bar{\kappa} = 0{\cdot}066$, $\lambda_0 = 3{\cdot}07\,\mu$, $\lambda_1 - \lambda_0 = 0{\cdot}29\,\mu$, and $\bar{\kappa} = 0{\cdot}123$, $\lambda_0 = 6{\cdot}15\,\mu$, $\lambda_1 - \lambda_0 = 0{\cdot}29\,\mu$. We shall use the values for each band to calculate the value of r.

For the first band,

$$\begin{aligned}\bar{\kappa} &= r^2\frac{0{\cdot}103}{3{\cdot}477\,b\theta_0} = r^2\frac{0{\cdot}103}{(3{\cdot}477\,a-\theta_1{}^2)}\\ &= r^2\frac{0{\cdot}103}{(\theta_0{}^2-\theta_1{}^2)} = r^2\frac{0{\cdot}103\,\lambda_1{}^2\lambda_0{}^2}{(\lambda_1{}^2-\lambda_0{}^2)\,4\pi^2v^2}\\ &= r^2\frac{0{\cdot}103\,\lambda_1{}^2\lambda_0{}^2}{(\lambda_1-\lambda_0)(\lambda_1+\lambda_0)\,4\pi^2v^2}.\end{aligned}$$

If r be measured in electromagnetic units v^2 cuts out. Write $\lambda_1 = \lambda_0$ except in the factor $\lambda_1-\lambda_0$. Then

$$r^2 = \frac{8\pi^2\bar{\kappa}\,(\lambda_1-\lambda_0)}{0{\cdot}103\,\lambda_0{}^3}.$$

Similarly, for the other band we obtain

$$r^2 = \frac{8\pi^2\bar{\kappa}\,(\lambda_1-\lambda_0)}{0{\cdot}500\,\lambda_0{}^3}.$$

On substituting for $\bar{\kappa}$, λ_1, and λ_0, we obtain from the first band $r = 7110$, and from the second $r = 1550$. As r denotes the elementary charge of electricity divided by the mass of the hydrogen atom it should be about 9660.

The model has thus been tested numerically on three independent points. It gives 2·32 for the ratio of the wave-lengths instead of 2·00, and it gives 7110 or 1550 for the value of e/m instead of 9660, according as we use the first or second band. If we consider the simplicity of the assumptions made, and the room there is for modification (*e.g.* making k different for the different linkings), the agreement must be regarded as gratifying.

The other maxima in the absorption spectrum are possibly due to more complex molecules.

This is incidentally the first time that chemical bonds have been connected mathematically with absorption bands.

Spectroscopic Investigations in Connection with the Active Modification of Nitrogen. II.—*Spectra of Elements and Compounds excited by the Nitrogen.*

By the Hon. R. J. Strutt, M.A., F.R.S., Professor of Physics, and A. Fowler, F.R.S., Assistant Professor of Physics, Imperial College of Science and Technology, South Kensington.

(Received November 13,—Read November 23, 1911.)

[Plate 6.]

Introductory.

In continuation of previous accounts of the active modification of nitrogen,* and of the spectrum of the afterglow which is associated with it,† the present paper gives further details of the spectra which are developed when various elements and compounds are introduced into the glowing gas. Preliminary investigations of the spectra were made by direct observation, and with a small quartz spectrograph, and when greater resolving power was required a larger quartz spectrograph and an instrument of the Littrow type were used.

The arrangements for producing the afterglow were as described in the previous papers. By means of a mechanical pump a stream of purified nitrogen at low pressure was passed through the discharge tube, and the afterglow was observed in a side tube, into which the various substances were introduced as required. It will be remembered that a discharge with condenser and spark gap is necessary to develop the afterglow with maximum intensity.

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* R. J. Strutt, Bakerian Lecture, 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 219.

† A. Fowler and R. J. Strutt, 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 377.

Later experiments have shown that the afterglow is also generated by the ring discharge produced by electromagnetic induction when the pressure of the nitrogen is appropriately adjusted. The spectrum of the exciting discharge is identical with that of the condensed discharge which has already been described; that is, the first positive bands of nitrogen are feeble, the second positive bands very intense (giving a bluish colour to the ring), the third positive group absent, and the fourth positive bands present.

We mentioned in our previous paper (p. 377) that the deep yellow afterglow was destroyed by a small amount of oxygen in the nitrogen employed, and that only a bluish-white luminosity was then visible. This is due, as we have since ascertained, to the formation of a small quantity of nitric oxide by combination of oxygen and nitrogen in the discharge; for the same effect is produced if a very small quantity of ready made nitric oxide is introduced into the stream *after* it has passed the discharge tube. Larger quantities introduce a different phenomenon—the yellow-green flame with continuous spectrum.* The effect of a small nitric oxide admixture is to suppress the α-group of afterglow bands, leaving the rest of the afterglow spectrum untouched.

Metallic Elements.

Sodium.—It has already been pointed out by one of us that when sodium is heated a little above its melting point in the presence of active nitrogen, the sodium spectrum is developed with great brilliancy; when heated more strongly, the vapour close to the metal becomes visibly green, and in this region the D lines almost vanish, while the pair of green lines about 5685† is shown very strongly. Other lines of the subordinate series are also very bright, and lines of potassium appear as impurities.

As regards the principal series, the photographs suggest that the suppression of the D lines does not so much indicate a tendency towards the extinction of this series as a change in the position of maximum intensity to the next pair of lines in the series near 3303, which is the strongest in the whole spectrum; other lines of the principal series at 2853 and 2680 are also well visible.

In the first subordinate series the greatest intensity is towards the red end, and the colour of the glowing vapour indicates that the maximum occurs at the green pair 5685. The second subordinate series is relatively very weak. Apart from the redistribution of intensity in the principal series, however, the spectrum approximates very closely to that given by sodium in the oxy-hydrogen flame or electric arc.

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* R. J. Strutt, 'Roy. Soc. Proc.,' in course of publication.

† Wrongly referred to in the Bakerian Lecture as the E line.

The suppression of the D lines recalls an experiment described many years ago by Lockyer,[*] in which a similar result was obtained. In this case an electric discharge was passed through a capillary tube which was in connection with a wider tube containing heated metallic sodium, the platinum electrode nearest to the metal being a few inches above it. There was no obstruction between the electrode and the sodium, and the only gas present was the hydrogen given off by the metal.

The similar results obtained in hydrogen and nitrogen suggested that in both cases the effect might be due to the production of the spectrum under reduced pressure. We have not, however, been able to produce the same phenomenon by passing a discharge through sodium vapour in a vacuum tube, although the lines of the subordinate series were well displayed under these conditions.

Potassium.—The photographed spectrum was rather faint, but it showed very clearly the lines of the principal series at 4046, 3447, 3217, and 3102, the first named being by far the strongest. Several lines belonging to the two subordinate series were shown faintly, and there were feeble indications of a band fading to the violet, with its head about 460.

Magnesium.—The spectrum of this metal was only observed with difficulty, and the photograph obtained was not very strong. Nevertheless it sufficed to show that the spectrum did not contain any of the characteristic spark lines, such as that at 4481·3. The characteristic flame line at 4571 appeared faintly, while the adjacent line at 4703, which is a much stronger line in the arc spectrum, did not appear. The spectrum thus approximates closely to that given by the flame, but it tends to be intermediate between the flame and the arc. The lines photographed are shown in the following table:—

Wave-length.	Intensity in glow.	Remarks.
4571·33	1	Characteristic flame line.
3838·44	10	1st line of triplet, 1st subordinate series.
3336·83	1	" " 2nd " "
3097·06	3	" " 1st " "
2852·22	2	" " 1st " "
2779·94	3	Arc line, not included in series.

The *b* group was observed visually, but was not photographed.

[*] 'Roy. Soc. Proc.,' 1879, vol. 29, p. 266.

Mercury.—The mercury line spectrum is well developed in active nitrogen, and the photograph shows all the stronger lines of the arc spectrum which are given by Kayser and Runge. With the exception of the pair 5790, 5769, and the line 4078, all the lines photographed belong to the two triplet series, and include numbers 4 and 5 of the first subordinate series, and numbers 3 and 4 of the second subordinate series. The relative intensities of the lines are not notably different from those of the arc spectrum. Comparisons with the spectrum of a mercury lamp revealed no distinct difference.

Thallium.—The chloride of the metal was employed in this experiment, but no bands special to the compound were observed or photographed. The glow produced was bright green, and the spectrum consisted of numerous sharply defined lines. With the exception of two probable impurity-lines at 3239, 3220, the lines agree very closely with those of the arc spectrum, as regards their relative intensities, but there are indications that the second subordinate series is somewhat weaker than in the arc.

Nickel.—Nickel chloride was used, but the only bands observed were afterwards found to be identical with those given by cuprous chloride, and they may therefore be referred to an impurity of copper in the substance employed. Some of the lines of copper were also shown in the photographs. In addition, between 20 and 30 lines due to nickel itself were photographed, and these are identical with the strongest arc lines of the metal, so far as they can be identified with the small dispersion employed. The lines were most distinct in the ultra-violet region, 3620 to 2900, where there were no copper bands to mask them.

The Halogens.

Iodine.—The vapour given off by iodine at ordinary temperatures readily generates a characteristic bright blue glow when it comes in contact with active nitrogen. The spectrum shows a broad faint band in the green, and a number of ill-defined bands in the blue and ultra-violet, of which one at about 3430 is by far the most prominent (Plate 6, fig. 1). In addition, there is an apparently continuous background, which is feeble on the less refrangible side of a band at 4770, but is quite strong from that wave-length to the most refrangible part of the spectrum shown on the photographs. The bands as a whole do not appear to have been previously recorded, but the strongest band has been noted by Könen,* who describes it as extending from 3430 to 3340. We have found, however, that the vacuum tube shows all the bands of the glow spectrum in the region compared (3200 to 5900), but the vacuum tube differs from the glow in showing greater luminosity in the less refrangible parts of the spectrum. Also, while the most intense band in the vacuum-tube is at 4310, that in the glow is at 3430. Details relating to the bands of the glow spectrum are given in the appended table.

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* 'Wied. Ann.,' 1898, vol. 65, p. 269.

Wave-lengths of Iodine Bands.

Approx. wave-length.	Intensity..	Approx. wave-length.	Intensity.
4770	5	2890	3
4620	3	2835	2
4310	5	2775	2
3890	2	2720	1
3535	1	2480	2
3495	1	2430	1
3430	10	2380	1
3270	2	2075	5

The last on the list, at 2075, is a strong sharp line, quite unlike the others in appearance, but there seems to be no reason to assign it to any impurity, as it has not been found in mercury or any other substance likely to be present.

The band at 4770 was photographed with the Littrow spectrograph, but there were no signs of resolution into fine lines in a spectrum of purity 3000 in that region.

It should be noted that the flutings shown in fig. 1, which only occupy the upper half of the spectrum, are due to nitrogen.

Bromine.—The luminosity in this case was very feeble, and the photograph of the spectrum shows only one band which can be attributed to bromine. This is a broad symmetrical band, having ill-defined edges about 2930 and 2890. A band in the orange, dominating the colour of the glow, was observed visually.

[*Note added December* 5.—This band is not identical with the yellow-green band recorded in the vacuum tube spectrum by Eder and Valenta. With moderate dispersion it was found to consist of eight narrow bands extending from about 5875 to 6070, at nearly equal distances of 28 tenth-metres.]

Lines of aluminium were well seen in this spectrum, the metal having been carried forward into the glowing gas, probably in the form of a volatile bromide.

Chlorine.—The spectrum of chlorine excited by active nitrogen was similar to that of bromine, but the single broad band shown on the photograph occurs in a more refrangible part of the spectrum, namely, 2600 to 2540. No lines of chlorine were recorded on the photograph.

Compounds of Metals.

Cuprous Chloride.—The blue-green glow developed by cuprous chloride gives a spectrum which is generally similar to that of the same substance when volatilised in the Bunsen flame. The afterglow, however, produces a greater number of lines of copper, and the band spectrum of the chloride is more completely developed. The chloride bands are also better visible in the glow than in the flame, in consequence of the absence of overlying continuous spectrum. A series of bands which is either absent from the flame, or is very weak, is a conspicuous feature in the glow spectrum. These bands are more refrangible than those which occur in the flame, their approximate wave-lengths being 4150, 4080, 4010, 3945, 3885, 3835, 3785, 3740. The intervals between the bands suggest that they form a connected series which is related to those in which the flame bands have been arranged by Kien.*

Chlorides of Tin.—Stannous and stannic chlorides produce a brilliant blue glow. The most striking feature shown on a photograph of the spectrum of stannic chloride is an intense band in the blue, extending from about 4000 to 5000; with small dispersion, the band shows no signs of any maxima, and fades off gradually in both directions (Plate 6, fig. 2). In addition there are seven lines of tin between 3262 and 2706, which are identical with the strongest lines of the arc spectrum in this region. There are other faint lines at the approximate positions 3855, 3780, 3748, 3480, and 3474, which have not yet been identified.

A photograph of the blue band, taken with the Littrow spectrograph, shows that it is not perfectly continuous. Superposed on the continuous background, there are several symmetrical but ill-defined bands, 4 or 5 tenth-metres broad, which show no further signs of resolution in a spectrum of a purity of about 4000 in the region where the bands occur. Accurate measures of these bands cannot be obtained, and it will suffice to state that there are 15 bands between 4768 and 4430, at nearly equal distances of 24 tenth-metres. Some of the bands are double. The bands are very similar in appearance to those which occur in fluorescence spectra, as, for example, that of uranium phosphate. An experiment was accordingly made in order to ascertain if a fluorescence could be obtained by the action of ultra-violet light on stannic chloride.

A small quantity of stannic chloride was placed in a quartz tube, 2 cm. in diameter, which was exhausted and sealed, the liquid chloride being frozen with liquid air during this operation. The quartz tube was then examined in a concentrated beam from an electric lantern with quartz condensers, with and without a deep violet glass. But no fluorescence could be observed, either at the ordinary temperature or when the tube was warmed.

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* 'Zeit. für Wiss. Photog.,' 1908, vol. 6, p. 337.

Experiments on the vacuum-tube discharge through the vapour of stannic chloride showed that the discharge was generally similar in colour to the glow produced in active nitrogen, but was not so perfect a blue. The vacuum-tube spectrum, however, showed the same strong blue band as the glow, but there was also a fairly bright continuous, or nearly continuous, spectrum extending from the blue band to the red. Lines of tin were also more prominent in the vacuum-tube than in the glow.

Mercuric Iodide.—This substance yields a violet glow, and the spectrum shows bands which appear to be characteristic of the compound, together with a feeble band which coincides with the principal band of iodine about 3430. Mercury was only represented by the line 2536·7, which was no stronger than in other spectra obtained in the same manner when mercury was only accidentally present.

The strongest band begins at about 4455. It is very intense from that point to 4390, after which it fades off rather rapidly to the neighbourhood of 3700. With the small resolving power employed, the band is a nearly continuous one, but there are indications of numerous ill-defined maxima. The spectrum, as a whole, is similar to that described by Jones,[*] and afterwards by Lohmeyer,[†] as occurring in mercuric iodide rendered luminous in a vacuum tube. For the brightest band the wave-length of the beginning is given by Jones as 4396, but from the description there can be no doubt that it is the same band as that found in the glow. Lohmeyer's wave-lengths, giving the brightest parts of the band as lying between 4456 and 4393, confirm this. The remaining (faint) bands agree with those tabulated by Jones.

Sulphur and its Compounds.

Sulphur.—When sufficiently heated in the glowing nitrogen, sulphur gives a blue glow. The spectrum consists of a succession of bands, degraded to the red, and very evenly distributed. Between 4700 and 2800 there are about 30 principal bands, some of which are complex groups or doublets. There was little or no continuous spectrum. The spectrum has nothing in common with that of sulphur in a vacuum tube, but it is closely related to that given by the flame of carbon disulphide burning in air. In the flame, however, the bands are superposed on a moderately strong continuous spectrum, and those which are more refrangible than 3400 are only very feebly displayed.[*] When the flame was supported by oxygen, it was found that the bands were barely visible, while another group in the region 3000 to 3200 (seen also in the flame of burning sulphur) was introduced.

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[*] 'Ann. d. Physik.,' 1897, vol. 42, p. 50.

[†] 'Zeit. für Wiss. Photog.,' vol. 4, p. 376.

Sulphuretted Hydrogen.—The spectrum obtained when sulphuretted hydrogen was introduced into active nitrogen was identical with that given by sulphur in the nitrogen.

Carbon Disulphide.—The spectrum given by carbon disulphide in nitrogen showed the bands already described as occurring with sulphur, but the bands were only well developed on the less refrangible side of 3700. The cyanogen band 3883 and the carbon line 2478 were shown feebly.

In the ultra-violet there was an additional series of well-marked bands, degraded to the red, having their heads about 2550, 2592, 2620, 2665, 2700, 2745, 2785, 2830, 2920. These bands were also present, in an ill-developed form, and superposed on continuous spectrum, in the carbon disulphide flame. They appeared also in the spectrum of impure sulphurous anhydride in a vacuum tube, while the less refrangible group previously described was absent.

Further investigations will be undertaken to determine whether the different groups of bands represent different compounds of sulphur, or sulphur in different molecular states.

Compounds of Carbon.

The introduction of many of the compounds of carbon into the nitrogen afterglow results in the development of the spectrum of cyanogen, and direct chemical evidence of the formation of cyanogen has been obtained.[†] The cyanogen spectrum was strongly developed in cyanogen, ethyl iodide, chloroform, carbon tetrachloride, and acetylene, and it was also seen, with less intensity, in methane, pentane, ethylene, alcohol, ether, and benzol. An investigation of the spectra thus obtained, however, has revealed some interesting peculiarities.

The cyanogen spectrum, as given by the flame of the burning gas, has long been recognised as consisting of two principal sets of bands. One of them occupies the red, yellow, and green parts of the spectrum, and the flutings composing the bands are degraded to the red. The other consists of groups of flutings in the violet and ultra-violet, degraded to the violet, which are especially well known in consequence of their great brilliance in the spectrum of the carbon arc. For convenience of reference, these two sets of bands may be distinguished as the red and violet groups respectively. In addition, there are four groups of fainter flutings in the ultra-violet, degraded to the red, which have been regarded as the probable "tails" of the violet bands.*

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[*] The chief bands of the CS_2 flame spectrum are about 3370, 3420, 3500, 3557, 3590, 3645, 3680, 3740, 3835, 3940, 4050, 4080, 4160, 4200, 4275, 4310, 4440, 4480.

[†] R. J. Strutt, *loc. cit.*, p. 228.

The different compounds of carbon do not all behave in the same way when in contact with active nitrogen. In most cases, the "flame" produced was of a lilac tint, very similar to that of the cyanogen flame, but in the case of carbon tetrachloride, or chloroform, the flame was orange in colour and more luminous, and the red spectrum of cyanogen was more strongly developed in relation to the violet.

The "Red" Bands.—In carbon tetrachloride (Plate 6, fig. 3) and chloroform the red spectrum is very brilliant, and is particularly free from contamination with other spectra. The photographs give only feeble indications of the stronger of the second positive bands of nitrogen, and they show no traces of carbonic oxide, or of the Swan bands of carbon. Moreover, the system of bands can be traced clearly into the blue-green and blue, where there are several easily visible bands which are not seen, or only seen with difficulty, in the ordinary flame or vacuum-tube spectrum. This method of producing the spectrum accordingly offers special advantages for the study of the regularity of the bands, and it has been utilised by Messrs. Fowler and Shaw in a separate investigation of the red cyanogen spectrum as obtained from different sources.† Previous accounts of this spectrum have been very incomplete, and only roughly approximate wave-lengths of the bands have been available.

In the small scale photograph reproduced in fig. 3, and in visual observations, the bands appear to follow each other at nearly equal intervals and to show no marked discontinuity as regards their intensities. Other photographs taken with shorter exposures, however, show that the principal bands occur in groups of three, of which the middle one is the brightest in each case. It has been found that all the bands can be arranged in seven regular series, similar to those which constitute the first positive band spectrum of nitrogen.

The Violet Bands.—The familiar cyanogen bands in the violet and ultra-violet are greatly modified in all the carbon compounds which produce a visible luminosity when they are brought in contact with active nitrogen.

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* King, 'Astrophys. Journ.,' 1902, vol. 14, p. 323; Jungbluth, 'Astrophys. Journ.,' 1904, vol. 20, p. 237.

† 'Roy. Soc. Proc.,' this vol., p. 118.

Considerable resolving power is necessary to show the character of the changes clearly, and the Littrow spectrograph was utilised in obtaining the comparative spectra which are reproduced on an enlarged scale in Plate 6, figs. 4 and 5. It will be seen that the details of the violet groups are very different in the glow as compared with the carbon arc.

Taking the 4216 band of the glow spectrum as a typical case, there is a modified development of the structure lines proceeding from the first and third heads (counting from red to violet, or right to left), and a partial suppression of the second and fourth heads. The structure lines emanating from the first head are identical with lines in the corresponding part of the arc band, but there is a conspicuous interruption of the sequence at a short distance from the head, after which the lines became stronger and overrun the second head, which itself appears to be rather weak. A similar effect is observed in the case of the third head, the structure lines of which overrun the fourth, but the third head is not nearly so strong as the first.

These effects are apparently identical with the variations in the negative band of nitrogen 3914, and in the cyanogen band 3883, which have been observed by Deslandres* as the pressure was reduced from one atmosphere to a few millimetres. We have confirmed this observation in the case of the first heads of the cyanogen bands 4216 and 3883, and the differences between the glow and arc bands, to which reference has so far been made, are therefore probably due, either directly or indirectly, to the fact that the cyanogen bands in the glow were produced at a relatively low pressure (5 to 10 mm.).

A still more striking difference between the glow and arc bands occurs in the most refrangible part of each of the violet groups. There is a special increase of intensity in this region, which may possibly be due to a local intensification of some of the series of structure lines, or to the introduction of entirely new bands. Until still greater resolving power can be employed, it will be difficult to determine the exact nature of the difference, but the development of new bands offers the simplest explanation. In favour of this view is the observation that the structure lines of the glow bands do not all occur in the bands of the arc, and also the fact that in some of the photographs (*e.g.* in cyanogen, Plate 6, fig. 6*a*) the supposed new bands are far stronger than the first heads of the groups. Assuming that new bands are developed, their less refrangible edges would be about 4495 (in the 4606 group), 4153 (in the 4216 group), and 3850 (in the 3883 group). Each band must then be supposed to consist of a group of close lines extending over about 9 tenth-metres, this group being followed by a gap of about 3 tenth-metres, and this again by another group of lines extending over about 10 tenth-metres. The "new" bands are especially intense in ethyl iodide, cyanogen, and acetylene; they are also well marked in ethylene and chloroform, but are not nearly so pronounced in carbon tetrachloride.

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* 'Comptes Rendus,' 1904, vol. 139, p. 1179.

Stimulation of cyanogen by the nitrogen afterglow is not the only means of producing these new bands, as they also appear on the photographs of the spectrum produced by the phosphorescent combustion of cyanogen in ozone.*

We have not yet succeeded in obtaining the new bands clearly in vacuum-tube discharges through cyanogen, but there were feeble indications of their presence when wide discharge tubes were employed.

Special care has been taken to show that the spectrum given by cyanogen itself in the nitrogen afterglow has the same peculiarities as that produced from other carbon compounds. When the cyanogen from mercuric cyanide is merely passed through a phosphorus pentoxide drying tube, the removal of water vapour is not complete, and the hydrocarbon band 4315 usually appeared in the spectrum obtained. It seemed possible, therefore, that the modifications of the violet bands in this case might result from the presence of hydrocarbons formed by interaction of water vapour with cyanogen. An experiment was accordingly made in which the cyanogen introduced into the afterglow had been kept in contact with the drying agent for five days. In this case (fig. 6*a*) the hydrocarbon band did not appear, but the violet cyanogen bands presented the same appearances as before. Hence, the stimulation of ready-made cyanogen by active nitrogen produces the same modifications of the violet bands as are observed when the gas is produced by the interaction of nitrogen with other carbon compounds which give luminous effects. The modified bands therefore do not represent cyanogen in course of formation, as might, perhaps, have been supposed. As previously suggested,† it would seem that cyanogen is immediately produced by admixture of the carbon compounds with active nitrogen, and that the observed spectrum is due to the subsequent stimulation of the gas by the peculiar conditions existing in the afterglow.‡

The Cyanogen "Tail" Bands.—The ultra-violet groups of flutings, fading towards the red, which have been regarded as tails of the violet groups, are also very considerably modified in the glow cyanogen as compared with their appearances in the carbon arc (Plate 6, fig. 6, where the bands in the arc are indicated by black dots). So far as can be determined from the photographs available, including some taken with the Littrow spectrograph, the bands are changed in the glow in the same manner as the first heads of the 4216 and 3883 groups; that is, there is an intensification of the structure lines near the head of each band, a conspicuous break in the sequence of the lines at a short distance from the head, and a greater development of the lines immediately following the break. It is probable that a complete investigation of the structure of these bands, in relation to the modified violet bands, would throw additional light on the supposed connection of the two groups, but it would be a laborious piece of work, and cannot at present be undertaken. In addition to the bands noted by King at 3910, 3945, 3985, there is evidently one near 3883, and another about 4030.

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* R. J. Strutt, 'Phys. Soc. Proc.' The "unknown" bands mentioned in this paper as occurring at 431 and 415 appear to be respectively the hydrocarbon band 4315 and the new band of cyanogen 4153. The cyanogen band 4606 is also represented by a band about 450, which would correspond with another of the new cyanogen bands.

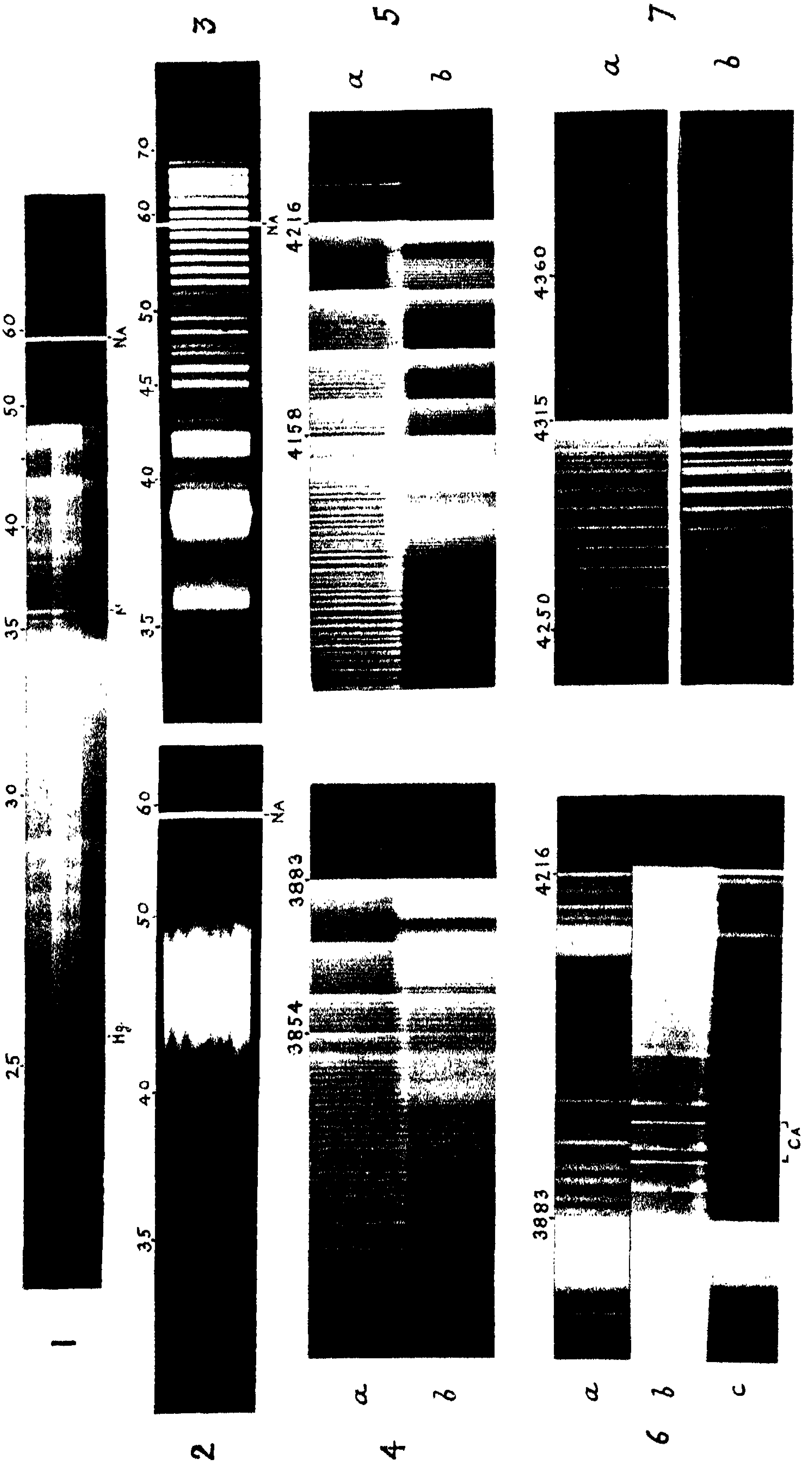
† R. J. Strutt, 'Roy. Soc. Proc.,' vol. 85, p. 228.

‡ It should be mentioned that the photographs of the spectrum generated by the specially dried cyanogen in the afterglow of nitrogen show two of the bands (4679 and 4365) of the "high pressure" spectrum observed in carbon monoxide by Fowler

The Hydrocarbon Band 4315.—The hydrocarbon band 4315 appeared in the glow spectrum in the case of carbon compounds which contain hydrogen, and in cyanogen which had not been completely freed from water vapour. Like the cyanogen bands, this also shows very considerable modifications as compared with the bands obtained from flames. This will be seen from Plate 6, fig. 7, in which the band given by the oxy-coal-gas flame is compared with that given by acetylene in nitrogen. No new lines appear in the glow band, but there are great differences in the relative intensities of the structure lines in the two spectra. Particularly striking is the concentration of luminosity about the head of the band at 4315. This is followed by a dark space about 5 tenth-metres broad, on the more refrangible side, after which there is a special intensification of the first half-dozen structure lines. On the less refrangible side, the flame line 4324 almost disappears in the glow, and the more refrangible members of the group lying between 4335 and 4390 are especially developed. The character of the change corresponds generally with that of the violet cyanogen bands, and of the negative band of nitrogen 3914, under reduced pressure, and the variations are possibly to be accounted for in the same manner.

('Monthly Notices R.A.S.,' vol. 70, p. 490). These bands had not then been observed in any other compound of carbon and were provisionally attributed to carbon monoxide; their presence in cyanogen may have been due to an impurity, or the real origin of the bands may be carbon. The bands in question are generally similar in structure to the new cyanogen bands 4495, etc., and it is remarkable that they occupy positions with respect to the bands of the Swan spectrum corresponding to those which the new cyanogen bands occupy with respect to the violet bands 460, 421, and 388.

SPECTRA DEVELOPED IN NITROGEN AFTERGLOW



Summary and Conclusions.

(1) The spectra generated by the nitrogen afterglow do not differ fundamentally from those which can be produced by other means of excitation. In many cases, however, band spectra are better displayed in the glow, and the more refrangible parts of the spectrum are more completely developed. The method therefore adds to our resources for the production of spectra.

(2) The spectra of metallic substances approximate to those obtained in the electric arc, or are intermediate between arc and flame spectra. In the case of sodium, when sufficiently heated, the maximum intensity in the principal series is at λ 3303, the D lines being nearly extinguished.

(3) The spectra given by iodine, chloride of tin, and mercuric iodide are very similar to those obtained from vacuum tubes. There is, however, a greater development of the more refrangible parts of the spectrum in the case of the glow.

(4) The band spectrum of cuprous chloride is more completely developed in the glow than in the Bunsen flame. It shows an additional series of bands in the ultra-violet which is probably related to the series which constitute the flame spectrum.

(5) The spectra exhibited by sulphur, sulphuretted hydrogen, and carbon disulphide consist of bands which are quite distinct from those given by sulphur in a vacuum tube, but resemble the bands of the carbon disulphide flame in air.

(6) The cyanogen spectrum which is developed in the glow by cyanogen and certain other compounds of carbon differs in several respects from that observed in the cyanogen flame or carbon arc. Some of the differences appear to be due to the production of the spectrum at a relatively low pressure in the glow. A new set of bands, occupying positions near the more refrangible edges of the violet groups, occurs in the glow spectrum, and has also been observed during the phosphorescent combustion of cyanogen in ozone.

DESCRIPTION OF PLATE.

(1) Spectrum of iodine in afterglow.

(2) Spectrum of stannic chloride in afterglow.

(3) Spectrum of cyanogen produced by carbon tetrachloride in afterglow.

(4), (5) The cyanogen bands 4216 and 3883; (*a*) as given by carbon arc in air; (*b*) as given by acetylene in the afterglow.

(6) A group of "tail" bands of cyanogen; (*a*) and (*c*) as given by cyanogen and carbon tetrachloride respectively in the afterglow; (*b*) as given by the carbon arc in air. The marked heads are 3910, 3945, 3985, 4030. The greater development of the new bands 4153, 3850, by cyanogen, as compared with carbon tetrachloride, is also shown.

(7) The hydrocarbon band 4315; (*a*) as given by the oxy-coal-gas flame; (*b*) as given by acetylene in the afterglow.

The Less Refrangible Spectrum of Cyanogen, and its Occurrence in the Carbon Arc.

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[Plate 7.]

Introductory.

In connection with Prof. Strutt's investigations of the interaction between the active modification of nitrogen and certain compounds of carbon,* it became necessary to compare the resulting spectra with the spectrum given by cyanogen under the more usual conditions of experiment. It was then discovered that while precise measurements of the well known bands in the violet and ultra-violet had been made by Kayser and Runge, only roughly approximate positions had been tabulated for the bands, degraded in the opposite direction, which appear in the less refrangible parts of the spectrum. In view of the interest of these bands, arising from their possible occurrence in association with the violet bands in certain celestial bodies, as well as from the regularity of their structure, a new series of measurements has been undertaken.

The spectrograph chiefly employed for the determination of positions was one of the Littrow type, giving a linear dispersion of 57 tenth-metres per millimetre at 6700, and 16·5 tenth-metres per millimetre at 4700, the length of spectrum between these points being 6·7 cm. A quartz spectrograph giving 2 cm. for the same range of spectrum was also utilised for ready comparison of the spectra obtained from different sources.

Sources of the Spectrum.

The spectrum has been obtained from different sources, as follows:—

Flame.—The cyanogen was prepared by heating mercuric cyanide, and after drying by passage through a tube containing phosphorus pentoxide it was burned at a glass nozzle. In some of the observations the flame was surrounded by a glass chimney into which a stream of oxygen was passed, and under these conditions the intensity of the spectrum was greatly increased.

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* 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 228.

Vacuum Tube.—On account of the rapid decomposition of the gas by the electric discharge, a constant stream was passed through the vacuum tube during the exposure of the plates, which amounted in some cases to more than three hours. An "end-on" tube was of necessity employed, because of the dark deposit of paracyanogen which is quickly formed on the walls of the tube in the path of the discharge. It was further necessary to remove and clean the glass or quartz plate through which the light was transmitted to the spectrograph, about once in 20 minutes.

As obtained in this way the bands were very brilliant, and with careful adjustment of the supply of gas the spectrum was more easily maintained than in the case of the flame.

Active Nitrogen.—Prof. Strutt has shown that when certain compounds of carbon such as acetylene and carbon tetrachloride are brought in contact with "active nitrogen," the resulting luminous glow or flame gives a brilliant spectrum of cyanogen. In the case of acetylene, the flame is of a lilac tint, like that of the burning gas, but with carbon tetrachloride the luminosity is orange in colour and the red spectrum of cyanogen is more strongly developed in relation to the violet. The cyanogen spectrum produced in this way from carbon tetrachloride offers special advantages for investigations of the regularity of the bands, in consequence of the better development of the more refrangible bands of the series, which are very feeble in the spectra obtained from the other sources. The violet cyanogen bands in this spectrum are considerably different in detail as compared with those given by the cyanogen flame or carbon arc.* For convenience of reference the cyanogen spectrum obtained by the aid of active nitrogen may be called the "glow-cyanogen" spectrum.

Description of the Spectrum.

The main features of the red-cyanogen spectrum, as seen with instruments of small dispersion, are well known. The spectrum consists of a succession of bands—degraded towards the red—which are especially intense in the less refrangible parts of the visible spectrum, and become generally weaker as the blue is approached (Plate 7, figs. 1 and 2). With adequate resolving power each band is seen to be composed of three flutings, the heads of which form a triplet with the narrower pair towards the red. On the more refrangible side of most of the triplets there is an additional faint head, separated from the first component by an interval slightly greater than that between the two closer members of the triplet. The triplets, however, are the most striking features of the spectrum when moderate dispersion is employed.

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* See Strutt and Fowler, 'Roy. Soc. Proc.,' this vol., p. 105.

The spectrum shows considerable variations according to the source from which it is obtained. As will be seen from the data given in Table I, the relative intensities of some of the bands are far from being identical in the different spectra. The band near D (5859) is a notable example, being strong in the vacuum tube and glow-cyanogen spectra, but weak in the flame. Also, the bands more refrangible than 5240 only occur as traces in the flame, but are shown with moderate intensity in the vacuum tube, and better still in the glow-cyanogen. A complete comparison of the spectra from the three sources, however, was complicated by the presence of bands belonging to other spectra in the case of the flame and vacuum tube. In both flame and vacuum tube the bands of the Swan spectrum of carbon appeared, and the hydrocarbon band 4315 was also usually present. The vacuum tube spectrum generally showed, in addition, the carbonic oxide bands 6079, 5610·26, 5198·33, and 4835·44, probably on account of the imperfect removal of water vapour. The vacuum-tube spectrum further differed from the flame spectrum in showing some of the nitrogen flutings, though as a result of the constant changing of the cyanogen in the tube the bands of the first positive group were only shown as feeble traces, and those of the second positive group were not strong enough to be troublesome in the region under investigation.

In accordance with many previous observations,* it was found that when the cyanogen flame was fed with oxygen the whole spectrum was greatly increased in brightness, and that the Swan bands were especially intensified (fig. 4, *a*). The relative intensities of the various cyanogen bands, however, were not greatly affected.

The spectrum produced by carbon tetrachloride in active nitrogen was practically free from contamination with other spectra. There were practically no indications of the hydrocarbon band 4315 or of the bands of the Swan or carbonic oxide spectra. Bands of nitrogen were present, but they were not strong enough to interfere with the identification of the cyanogen triplets.

It should be remarked further that the visibility of the fainter triplets varied greatly with the source and with the dispersion of the instrument employed. In some cases these faint bands were masked by the structure lines emanating from adjacent stronger heads.

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* *E.g.*, Morren, 'Ann. de Chim. et de Phys.,' 1865, series 4, vol. 4, p. 312.

Determination of Wave-Lengths.

The bands in the extreme red were observed visually, and the positions of those less refrangible than 7000 were determined by the use of a wave-length spectroscope.

For the part of the spectrum more refrangible than 7000 the wave-lengths were determined from photographs taken with the Littrow spectrograph, the iron arc being used as a term of comparison. Sufficient iron lines were included in the measures to indicate the corrections to be applied to the wave-lengths calculated by the use of the Cornu-Hartmann formula.

It should be explained that the wave-lengths tabulated can only be regarded as close approximations. As in the case of flutings in general, there is evidence that the heads are complex groups of lines, and the measured wave-lengths will, therefore, depend to some extent upon the dispersion and resolving power of the instrument employed. In order to obtain a consistent system of wave-lengths for discussion of the regularity of the bands, the values tabulated, with the exception of those for the bands in the extreme red, were obtained from a single photograph of the spectrum of "glow-cyanogen," in which the dispersion at D was 38 tenth-metres per millimetre, and the purity of the spectrum at the same place 4000 (fig. 1). Spectra of greater purity were also obtained, but the identification of the heads was in some cases less certain on account of the interference of structure lines belonging to adjacent flutings.

An attempt has been made to include all the fainter bands so as to make the investigation of the structure of the spectrum as complete as possible. Some of the heads would not have been identified as such if their existence had not been indicated by the arrangement of the bands in series.

The positions of the various bands are indicated in Table I. Column 1 gives the wave-lengths, Columns 2, 3, and 4 the relative intensities in the flame, vacuum-tube, and glow-cyanogen spectra respectively, as roughly estimated on a scale of 10 for the brightest band; Column 5 shows the oscillation frequencies *in vacuo*; Column 6 indicates the series to which each band belongs according to the analysis which is given later, and Column 7 the difference (in frequency) between the value observed and that calculated from the series equation.

Table I.

Wave-length.	Intensity.			Oscillation frequency (*in vacuo*).	Series.		O−C.	Remarks.
	Flame.	Vacuum tube.	Glow-cyanogen.		*p.*	*m.*		
7435				13446	76	63	+4	Most refrangible head of a band observed visually.
7283				13727				Visual observations.
7273				13746				
7259				13772	77	64	0	
7119				14043				Visual observations.
7110				14061				
7091				14098	78	65	−4	
6961·6		1	1	14361	74	60	−2	Probable most refrangible head of a faint triplet.
6954·9	2	2	1	14374				
6946·0				14393				
6928·2				14430	79	66	−3	
6818·2	<1	2	3	14663				Also a faint head at 6780·2 (14745).
6809·8				14681				
6793·1				14717	75	61	−2	
6657·2	4	9	7	15017				Also a faint head at 6621·4 (15098).
6648·7				15036				
6632·2				15074	76	62	−1	
6503·0	9	10	10	15373				Also a faint head at 6467·3 (15458).
6494·7				15393				
6479·3				15430	77	63	−1	
6457·0		1	1	15483				
6448·9				15502				
6433·3				15540	73	58	+2	
6355·5	10	9	6	15730				
6347·9				15749				
6332·8				15786	78	64	−1	
6301·8		1	2	15864				Also a faint head at 6272·5 (15938).
6294·3				15883				
6280·0				15919	74	59	0	
6214·4	6	4	1	16087				
6206·7				16107				
6192·3				16145	79	65	+2	
6154·1	<1	3	3	16245				Also a faint head at 6124·4 (16324).
6147·4				16263				
6133·6				16299	75	60	−1	
6013·5	2	6	6	16625				Also a faint head at 5984·9 (16704).
6006·9				16643				
5993·5				16680	76	61	−2	

Table I—*continued.*

Wave-length.	Intensity.			Oscillation frequency (*in vacuo*).	Series.		O − C.	Remarks.
	Flame.	Vacuum tube.	Glow-cyanogen.		*p.*	*m.*		
5866·2		<1	<1	17041	73	57	0	Probable most refrangible head of a faint triplet; other components masked by next band.
5878·3				17007				Also a faint head at 5850·6 (17078).
5872·2	2	9	9	17025				
5858·7				17064	77	62	0	
5749·3				17389				Also a faint head at 5722·4 (17470).
5743·3	5	7	7	17407				
5730·8				17445	78	63	−1	
5747·9				17393				Superposed on previous stronger triplet, and not separately observed with small dispersion.
5742·2		1	1	17410				
5729·1				17450	74	58	−1	
5625·6				17771				Overlapped by next band. Both are involved in the 5635 band of the Swan spectrum in the flame and vacuum tube.
5619·4		2	2	17791				
5607·3				17828	79	64	0	
5616·3				17800				Also a faint head at 5591·2 (17880).
5611·1	3	3	4	17817				
5598·9				17856	75	59	0	
5490·8				18207				Also a faint head at 5467·4 (18285).
5485·5	2	5	5	18225				
5474·1				18263	76	60	−1	
5370·9				18614				Also a faint head at 5348·4 (18692).
5365·6	2	4	6	18632				
5354·8				18670	77	61	−2	
5255·4				19023				Also a faint head at 5233·2 (19104).
5250·7	2	3	5	19040				
5240·2				19078	78	62	−1	
5171·6				19331				Also a faint head at 5150·4 (19411).
5167·5			1	19346				
5156·3				19388	75	58	+2	These are superposed on the 5165 band of the Swan spectrum in the flame and vacuum tube.
5144·9				19431				
5139·6			1	19451				
5130·3				19487	79	63	0	
5058·2				19765				
5054·2		1	1	19780				
5043·7				19821	76	59	+1	
4949·7				20198				Also a faint head at 4931·3 (20273).
4945·9	1	2	3	20213				
4936·4				20252	77	60	0	

Table I—*continued.*

Wave-length.	Intensity.			Oscillation frequency (*in vacuo*).	Series.		O−C.	Remarks.
	Flame.	Vacuum tube.	Glow-cyanogen.		*p.*	*m.*		
4845·9	1	?	4	20630				Also a faint head at 4828·3 (20706).
4842·3				20646				
4833·2				20685	78	61	−1	
4798·1			1	20836				
4794·6				20851				
4785·5				20891	75	57	+1	
4746·0			2	21065				
4742·3				21081				
4733·3				21121	79	62	+1	These are superposed on the 4737 band of the Swan spectrum in flame and vacuum tube.
4694·6			2	21295				
4691·3				21310				
4682·6				21350	76	58	0	

In addition to the bands given in Table I, there were indications of fainter bands, the wave-lengths of which could not be satisfactorily determined from the photographs available. The arrangement of the bands in series, however, permits the calculation of the positions of these faint bands, and for completeness, the calculated wave-lengths of the more refrangible heads are stated below.

Fainter Cyanogen Bands.

Wave-length (air).	Frequency (*in vacuo*).	Series.	
		p.	*m.*
5398·4	18519	78	56
5274·8	18953	74	57
5005·6	19972	78	55
4893·2	20431	74	55
4584·0	21809	77	59
4489·5	22268	78	60
4398·8	22727	79	61
4283·3	23340	77	58

Series Relationships.

The triplets comprising the spectrum appear to be essentially similar to each other, and equally spaced, or nearly so, when estimated on the scale of oscillation frequencies. In the discussion of the distribution of the bands it will therefore suffice to consider the more refrangible members of the triplets.

An analysis of the frequencies has shown that the bands can be arranged in series which are similar to those in which the first positive bands of nitrogen have been arranged by Cuthbertson* and Deslandres.† This is shown in Table II, from which it will be seen that the bands form series of the usual type, whether taken in vertical or horizontal order. The bands in any single series are closely represented by Deslandres' formula, $n = \mathrm{A} + \mathrm{B}m^2$, in which A and B are constants, and m is a number increasing by unity for successive values of n.

If we consider, say, the vertical series, it is clear that the equation calculated from one of them should be applicable to the remainder by a mere change in the value of A, and the figures show that A will vary in such a manner for the different series that it can be represented by another equation of the same form. Hence, all the bands may be included in Deslandres' general equation

$$n = \mathrm{A} + \mathrm{B}m^2 - \mathrm{C}p^2.$$

Table II.—Regularity of Cyanogen Bands (oscillation frequencies *in vacuo*).

p …	79		78		77		76		75		74		73
m.													
66	14430												
	1715												
65	16145	2047	14098										
	1683		1688										
64	17828	2042	15786	2014	13772								
	1659		1659		1658								
63	19487	2042	17445	2015	15430	1984	13446						
	1634		1633		1634		1628						
62	21121	2043	19078	2014	17064	1990	15074						
			1607		1606		1606						
61			20685	2015	18670	1990	16680	1963	14717				
					1582		1583		1582				
60					20252	1989	18263	1964	16299	1938	14361		
							1558		1557		1558		
59							19821	1965	17856	1937	15919		
							1529		1532		1531		
58							21350	1962	19388	1938	17450	1910	15540
									1503				
57									20891				

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* 'Phil. Mag.,' 1902, [6], vol. 3, p. 348.

† 'Compt. Rend.,' 1902, vol. 134, p. 747.

The coefficients B and C, which are equal to half the second differences in the vertical and horizontal columns respectively, appear to have the same value in the case of cyanogen, and the general equation may therefore be written in the simplified form

$$n = \mathrm{A} - \mathrm{B}(p^2 - m^2).$$

By the use of this equation, a greater range of values of m may be utilised than in calculations based on a single series, and a more accurate representation of the several series may be expected on account of reduced extrapolation. In the actual calculation all the bands have been used in the determination of the constants, and the resulting equation may be written

$$n = 12{\cdot}90\,[(p+0{\cdot}6)^2 - (m+0{\cdot}8)^2] - 9741.$$

For the bands tabulated, p ranges from 73 to 79, and m from 56 to 66, and, as will be seen from the values O − C (observed *minus* computed) given in Table I, the equation represents all the bands very closely, and probably within the limits of error.

Occurrence in the Carbon Arc.

The occurrence of the violet and ultra-violet cyanogen bands (4606·33, 4216·12, 3883·55, 3590·48) in the spectrum of the arc between carbon poles at once suggests that the less refrangible bands under consideration should also appear in company with them. Hitherto, however, their presence does not seem to have been recognised.

Besides the violet and ultra-violet bands of cyanogen, and the Swan bands of carbon (5635·43, 5165·30, 4737·18, 4381·93), the carbon arc shows an immense number of fine lines in the yellow and red, which, so far as we are aware, have not previously been assigned to any definite substance. These lines evidently belong to a banded spectrum, although no distinct heads of flutings are recognisable with the instruments of high dispersion which are most frequently employed for so bright a source (see Plate 7, fig. 5). In observations with small dispersion, however, the lines are seen to be much more densely crowded together in certain places, giving the appearance of ill-defined bands, and comparison photographs, such as those in Plate 7, fig. 4, indicate that these brighter places in the arc spectrum coincide in position with the heads of cyanogen bands. All the chief cyanogen bands from the extreme red to that at 5240 can easily be traced in the arc spectrum in this way.

Conclusive evidence of a close relation between the two spectra is furnished by comparisons obtained with the Littrow spectrograph to which reference has been made. The resolving power of this instrument is sufficient to show a great number of the lines composing the cyanogen bands, while the dispersion is not too great to obscure the corresponding maxima in the spectrum of the arc. The photographs (Plate 7, fig. 2) show very clearly that not only are the brightest places in the arc spectrum coincident with the heads of the cyanogen bands, but that the structure lines are, for the most part, the same in both cases. From the red, as far as the Swan band 5635, the coincidences are very numerous, and some of the separate heads in the cyanogen flutings can be traced in the arc when the cyanogen spectrum is made use of as a guide; the three heads of the band 6333 are especially distinct in the arc spectrum. The comparison clearly indicates that the highly complex spectrum of the carbon arc in the red and yellow is, in the main, due to cyanogen.

The correspondence between the two spectra, however, is not complete when the cyanogen spectrum is obtained from a vacuum tube. While the vacuum-tube spectrum shows comparatively clear spaces between sharply defined bands, the arc spectrum exhibits an unbroken succession of lines with only ill-defined maxima to mark the positions of the heads of the bands. It would thus appear that the condition of the glowing gas in the arc is not identical with that of the gas in the vacuum tube. Other comparisons have shown, however, that a closer resemblance to the arc spectrum is given by the flame of cyanogen, either when the gas is burning in ordinary air or fed with oxygen. In this case the bands are less clearly separated than in the vacuum-tube spectrum, and the heads are less distinctly marked, when the dispersion is sufficient to resolve the bands into their component lines (Plate 7, fig. 3). Further, the arc bands, as a whole, are more like those of the flame spectrum in intensities than those of the vacuum tube, the variation of the band near D being especially noticeable. It is probable that the greater similarity between arc and flame than between arc and vacuum tube is to be attributed to the nearer equality of pressure conditions, as some band spectra are known to vary with pressure.*

Experiments on the changes in the spectrum when the arc is surrounded by different gases have yielded additional interesting evidence as to the cyanogen origin of the less refrangible part of the arc spectrum. The arc was enclosed in a glass globe, provided with arrangements for exhaustion, and for the admission of any desired gas.† When the globe was merely evacuated, hydrogen was liberated as the poles became heated, and the arc was then passing in rather impure hydrogen at a pressure of a few millimetres. Under these conditions, the violet bands of cyanogen were much reduced in intensity, and the many-lined spectrum in the yellow and red practically disappeared (fig. 6, *d*), as would be expected on the supposition that this spectrum is due to cyanogen. Hydrogen was itself represented by H_α, etc., and numerous lines of the secondary spectrum, and the hydrocarbon band 4315, which is not seen in the arc in air, was also present. The Swan band 6188 was also at times well developed in the spectrum, presumably because it was rendered more visible by the removal of the cyanogen band lines, on which it is superposed when the arc is observed in air. It would thus appear that the nearly total removal of nitrogen from the vicinity of the carbon poles results in the disappearance of the great majority of the lines in the yellow and red, and thus supports the view that this part of the spectrum of the carbon arc in air is mainly due to cyanogen.

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* Deslandres, 'Compt. Rend.,' 1904, vol. 139, p. 1174.

† See 'Phil. Trans.,' 1909, A, vol. 209, p. 449.

When the arc was passed in oxygen, either at atmospheric or at reduced pressure, the lines in question again disappeared, or nearly so, and the violet bands of cyanogen were weakened as in the previous experiment (fig. 6, *b*). At the same time, the Swan bands in the green were brightened, the orange band 6188 was easily photographed, and another band of the Swan spectrum less refrangible than H_α was occasionally observed. Both the orange band and the less refrangible one doubtless contribute to the spectrum of the carbon arc in air, but even the group beginning at 6188 can only be traced with difficulty. Bands of carbonic oxide, 5610, 5197, etc., were also occasionally seen when the arc was passed in oxygen, and in some of the observations of the arc *in vacuo*.

A similar experiment with chlorine surrounding the arc also indicated that the band lines under consideration were not produced in the absence of nitrogen.

There is accordingly abundant evidence to show that the great majority of the multitude of lines observed in the less refrangible part of the spectrum of the carbon arc in air are due to cyanogen, while a few of them represent the Swan spectrum of carbon. Bands of carbon and cyanogen thus account completely for the arc spectrum as observed under ordinary conditions.

Comparison with Celestial Spectra.

Among celestial bodies the violet bands of cyanogen have been observed in the spectra of the sun, stars of Secchi's fourth type, and comets. The laboratory experiments have given no evidence that the violet bands can exist apart from the red bands, except to an extent that can be accounted for by the greater intensity of the violet groups. Hence, when the violet bands appear with sufficient intensity in any source, the less refrangible bands may also be expected.

The presence of the ultra-violet band of cyanogen 3883 in the solar spectrum was first shown by Lockyer,* and the tables of Rowland indicate that the bands 4216 and 3590 are also represented among the Fraunhofer lines. All the bands, however, are feeble in the sun, and although the appearance of the less refrangible groups was scarcely to be expected, it nevertheless seemed desirable to make the comparison. Wave-lengths of the necessary degree of accuracy were obtained from photographs of the carbon arc taken with the ten-feet concave grating (fig. 5). Although the heads of the cyanogen flutings cannot be recognised in such photographs, accurate wave-lengths of the lines composing them can be obtained. Portions of the arc spectrum in the neighbourhood of the chief cyanogen bands were measured in detail and compared with the solar lines tabulated by Rowland, but no systematic coincidences could be established. The cyanogen spectrum thus appears to be too feebly developed in the sun to give appreciable indications of the less refrangible system of bands.

A photographic investigation of the Type IV stars made by Hale, Ellerman, and Parkhurst† has demonstrated the presence in the spectra of these stars of the violet bands of cyanogen, in addition to the Swan bands of carbon which were previously identified by Secchi in the visible spectrum. A number of narrow bands in the red and yellow, previously noted by Dunér and Vogel, were also shown in a photograph of the spectrum of 152 Schjellerup, but no significant coincidences with the less refrangible group of cyanogen can be certainly established. As in the solar spectrum. the violet bands do not appear to be sufficiently developed in this star to give much expectation of the visible manifestation of the red and yellow bands. Further comparison should be made when details of the red part of the spectrum become available for those stars of the fourth type in which the violet bands are more strongly developed.

As regards comets, bands in the red have occasionally been noted, but no accurate data are available.

Summary.

1. Revised wave-lengths are given for the bands forming the less refrangible part of the cyanogen spectrum. Numerous bands which have not previously been recorded are included.

2. The heads of the bands can be arranged in regular series similar to those constituting the first positive band spectrum of nitrogen.

3. There are considerable variations in the relative intensities of the

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* 'Roy. Soc. Proc.,' 1878, vol. 27, p. 308.

† 'Pub. Yerkes Observatory,' 1904, vol. 2.

various bands, according as the spectrum is obtained from the flame of the burning gas, from a vacuum tube, or from the luminous glow produced by the interaction of certain compounds of carbon with active nitrogen.

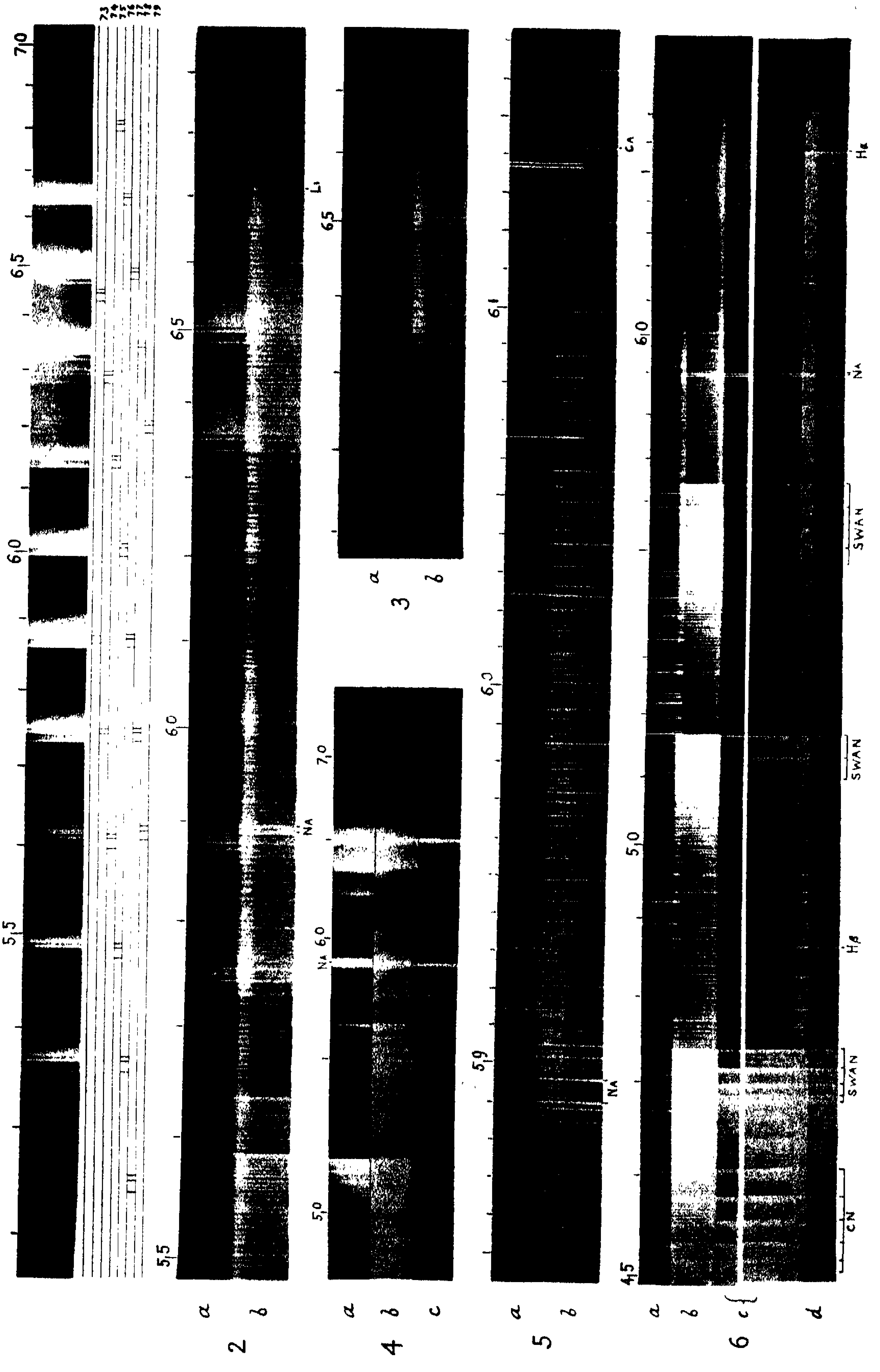
4. The complex spectrum of the carbon arc in the red and yellow is almost entirely due to cyanogen.

5. The spectrum of cyanogen in the sun is not of sufficient intensity to give visible indications of the red and yellow bands. Adequate data for comets and Fourth Type stars are not available for comparison.

DESCRIPTION OF PLATE.

1. Cyanogen spectrum produced by carbon tetrachloride in active nitrogen.
2. (*a*) Vacuum-tube spectrum of cyanogen.
    (*b*) Carbon arc comparison.
3. (*a*) Portion of flame spectrum of cyanogen.
    (*b*) Carbon arc comparison.
4. Small dispersion photographs—
    (*a*) Cyanogen flame fed with oxygen.
    (*b*) Carbon arc.
    (*c*) Cyanogen produced by CCl_4 in active nitrogen.
5. (*a*) Iron comparison spectrum.
    (*b*) Carbon arc (with 10 feet concave grating, 1st order).
6. (*a*) Iron comparison spectrum.
    (*b*) Carbon arc in oxygen at 10 in. pressure.
    (*c*) Carbon arc in air.
    (*d*) Carbon arc *in vacuo* (*i.e.*, hydrogen, etc.).

SPECTRA OF CYANOGEN AND CARBON ARC.

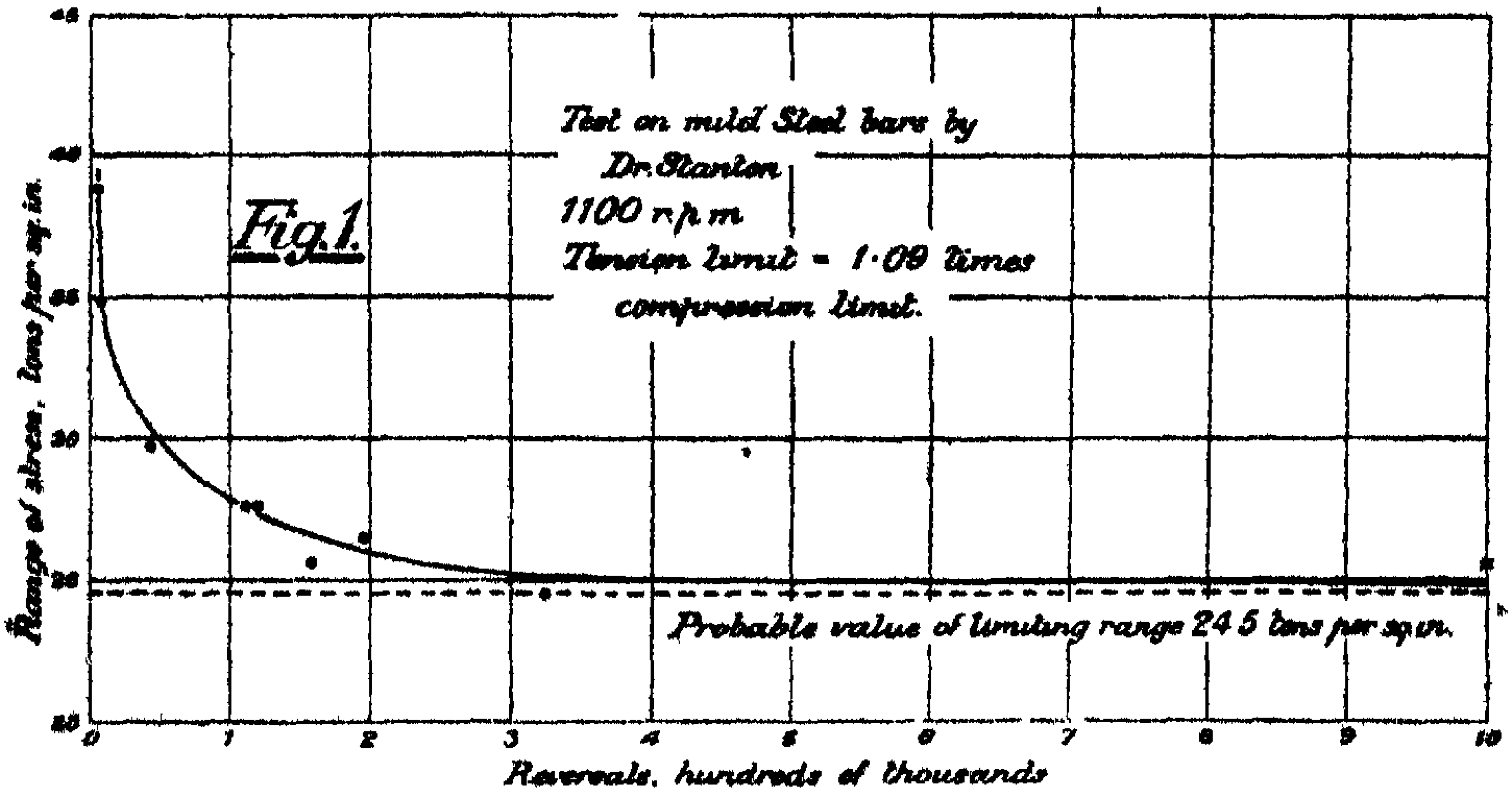


A High-Speed Fatigue-Tester, and the Endurance of Metals under Alternating Stresses of High Frequency.

By Bertram Hopkinson, F.R.S.

(Received November 20,—Read November 23, 1911.)

The deterioration of metals under the action of stress varying rapidly between fixed limits has been the subject of much experimental investigation. It is found that the important factor in the rate at which this "fatigue" goes on is the algebraic difference of the limits between which the stress varies, usually called the "range of stress"; and that the absolute position of these limits matters little, provided, of course, that the mean stress is not too large. The number of applications of a given range of stress required to fracture the piece increases as the range is diminished, the general nature of the relation between the two being as shown in the curve (fig. 1), which represents the results of a series of tests made by Dr. Stanton on mild steel. In these observations the stress alternated between compression and tension, the ratio of the compression and tension limits being 1·09. The form of the curve suggests that a range of stress not much below 25 tons, which in an average specimen would just cause fracture after a million reversals, could never break the bar, however often applied. One of the chief objects of the fatigue tests hitherto made has been to discover this "limiting range."



At an early stage in these investigations the question was raised whether the endurance by the material of a given cycle of stress is affected by the rate of repetition of the cycle. Besides its intrinsic interest, this question is of importance because on the answer to it depends the possibility of reducing the excessive amount of time taken to carry out fatigue tests. The determination within a few per cent. of the limiting range requires several separate tests in which the cycle is repeated at least a million times, and even that number is not always sufficient to give a reasonably close approximation. Wöhler worked with 60 to 80 reversals per minute, and he found that the same wrought iron which could just sustain a million applications of a range of 23 tons broke after 19 million repetitions of a range of 17½ tons. The more recent machines have been run at much higher speeds, and there is now a machine of the Wöhler type at the National Physical Laboratory which gives 2000 cycles of bending stress per minute. Even at this speed, which I believe is the highest yet reached under conditions admitting of accurate measurement, it takes eight hours to do a million reversals.

Within these limits it does not appear that frequency of application has much effect on endurance, that is, it takes the same number of repetitions of stress alternating between given limits to rupture a bar whether they be performed fast or slow. It is true that the experiments of Reynolds and Smith* suggested that endurance was less at high speeds, but this has not been confirmed by more recent work.† The weight of evidence seems to favour the conclusion that speed is without effect on endurance, at any rate up to 2000 applications per minute.

For reasons which I discuss in detail below I think that this independence of endurance and speed is to be expected *a priori* so long as the speed does not exceed a certain limit, but that if that limit be passed the number of repetitions of a given range required to produce fracture will begin to increase, and it seemed probable that the increase might become noticeable if the speed were so high as 7000 per minute. It was mainly with the object of testing this point that I constructed the machine described in this paper, which gives alternations of stress at the rate of over 7000 per minute, or three times as fast as the highest speed hitherto attained. I may say at once that, in the case of the mild steel which has been examined, the endurance is undoubtedly greater at the higher speed, not only in number of reversals, but also in the actual time taken to produce fracture. Hence the machine does not, as I thought it might (if the speed effect revealed were zero or small), serve the practical purpose of reducing the time required for fatigue tests. It seems rather to open a new field for investigation, which differs from that covered by the older slow-speed machines.

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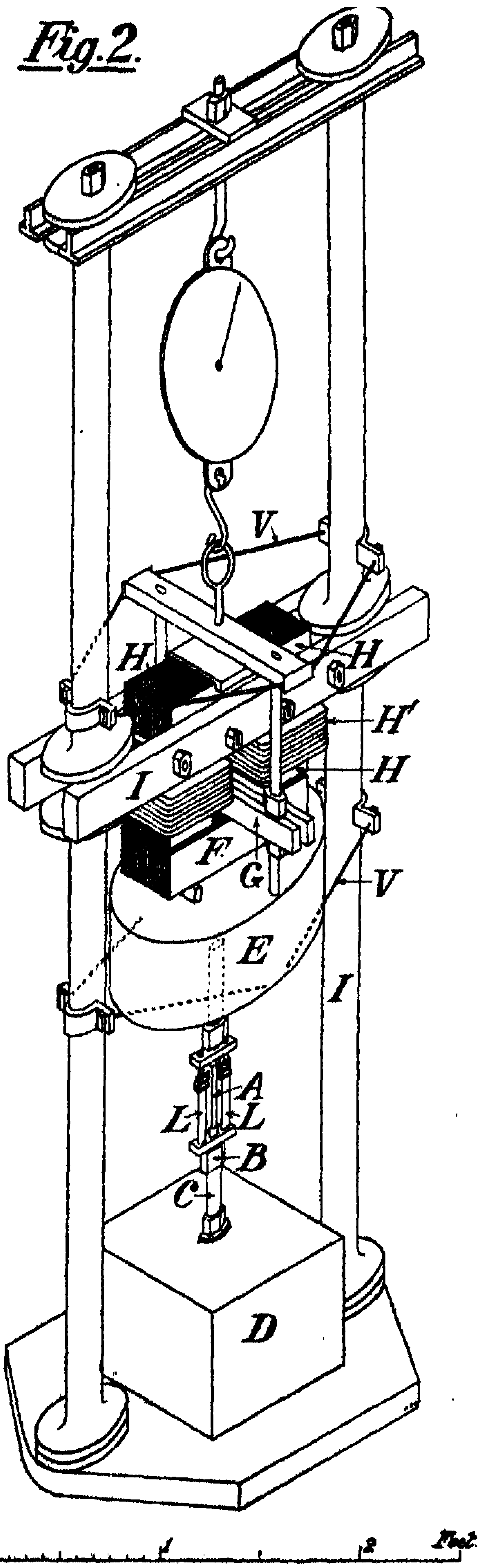
* 'Phil. Trans.,' A, vol. 199, p. 265.

† See "The Endurance of Metals," by Messrs. Eden, Rose, and Cunningham, Institution of Mechanical Engineers, October 20, 1911.

Description of the Machine.

The apparatus (which is shown semi-diagrammatically in fig. 2) is designed to give alternations of direct stress between any desired limits of tension and compression at the rate of 100 complete cycles per second, or more. The test-piece A is fixed at the lower end, by means of a nut B, to the screwed pillar C, which again is fixed into a massive block of cast-iron D, forming part of the base. The base is bolted to a concrete foundation. At its upper end the test-piece carries an iron weight E (about 180 lbs.), to the upper side of which is fixed the laminated armature F by means of yokes G. An electro-magnet H is carried by the pillars and cross-pieces I, above and independently of the armature, so as to leave a small air-space across which the magnetic pull acts. The magnet is excited by alternating current in the winding H′ and exerts a periodically varying pull along the axis of the piece, whose frequency is twice that of the current.*

Fig. 2.



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* When the experiments described in this paper were practically complete I learnt that Prof. Kapp had also

The test-piece behaves as a spring, the lower end of which is held fixed by the inertia of the masses to which it is attached, while the upper end carries the mass E. The adjustments are such that the natural period of vertical oscillations of this system is nearly equal to the period of the varying magnetic pull. The latter then sets up large forced oscillations of its own period. If the two periods are so far different that the dissipative forces have not much effect, the amplitude of the range of pull experienced by the piece is to the range of pull exerted by the magnet approximately in the ratio $1/(1-n^2)$, where n is the ratio of the two periods. The range of stress in the piece can be adjusted coarsely by variation of the frequency of the magnet current, and more finely by changing the E.M.F. applied to the coils.

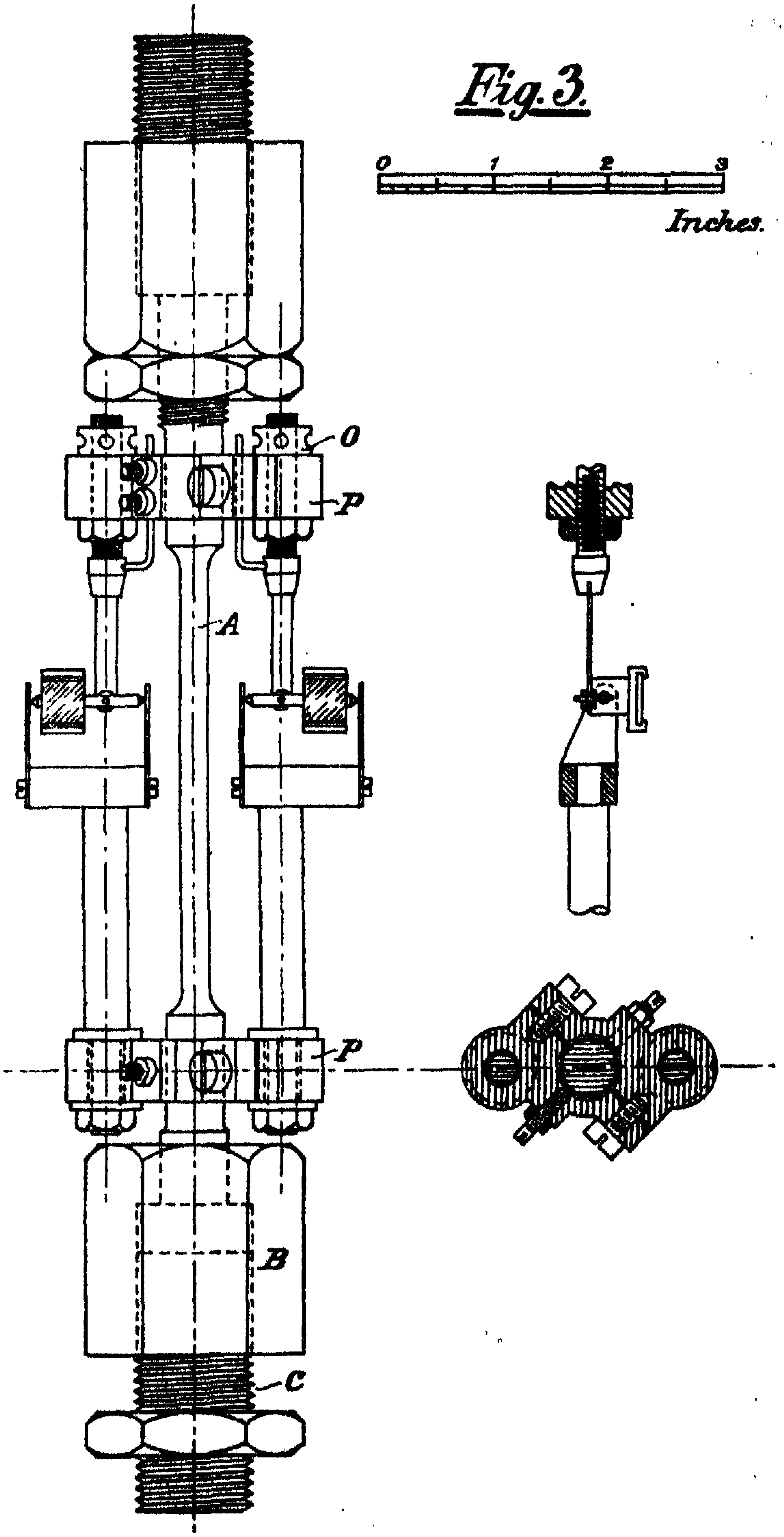
By means of wire guys V the weight is constrained to move parallel to the axis of the piece. Owing to the smallness of this movement the wires exert no appreciable pull in a vertical direction. The weight is carefully balanced so that its centre of gravity is in the axis of the test-piece.

The extension of the piece is measured by means of a pair of extensometers L, which are shown in greater detail in fig. 3. The concave mirror of each of these instruments casts on to a transparent scale an image of a horizontal lamp filament. When the instrument is in action the line image is drawn out into a band, whose ends are sharply defined, and whose length measures the range of extension in the piece. The extensometer readings are calibrated by means of the micrometer screws O (fig. 3), and were checked when the machine was in action by observing, with microscopes, the movement of needle points attached to the blocks P, P. The extensometer always agreed with the microscopes within 3/10,000 inch, or 3 per cent. of the range, and the measurements of extension are certainly correct within that amount.

The form of test-piece used is shown in fig. 3 with the extensometers attached. The section is 0·049 square inch. Current is supplied to the machine from a 4-pole rotary converter, which takes continuous current at 100 volts from a storage battery. Constant frequency in the supply of alternating current is, of course, of vital importance, and this is perfectly secured if the converter is driven from a battery which is not being charged or doing other work. The converter has a weak field, and is therefore largely self-compensating as regards speed, a drop in battery voltage producing a

constructed a fatigue-tester, in which direct stress was produced by the pull of an electromagnet excited by alternating current. The principle of resonance is not, however, used in this machine. A description of Prof. Kapp's machine appeared in the 'Zeitschrift des Vereines Deutscher Ingenieure,' Aug. 26, 1911.

Fig. 3.



corresponding drop in the field current. It is found that, once set going, the machine will continue to run for several hours, giving a constant stress within 2 per cent., without being touched in any way. The converter takes about 10 ampères at 100 volts when the machine is in action. Test-coils of 100 turns each of fine wire placed round the magnet poles, just above the air-gap, are connected to an electrostatic voltmeter, and serve to measure the flux density, whence the magnetic pull can be calculated.

Typical curves showing the relation between frequency of supply current and the corresponding stress for a given magnetic pull are given in fig. 4. The pressure of supply was raised in each case in proportion to the frequency, so that the flux density, and therefore the range of pull applied by the magnet, remained constant. The frequency was accurately measured by counting the beats between the notes produced by the machine and by a standard tuning fork. In one case (D_1) the maximum pull produced in the piece at the point of resonance was about 75 times, and in another (UB) (taken under similar conditions) 35 times the magnetic pull. The ratio between these quantities at the resonance point depends mainly on the rate of dissipation of energy by elastic hysteresis in the test-piece and its attachments, and by vibrations communicated to the ground. A bar of steel subjected to alternations of stress at the rate of 100 cycles or more per second in this machine gets perceptibly warm even when the stress is apparently within

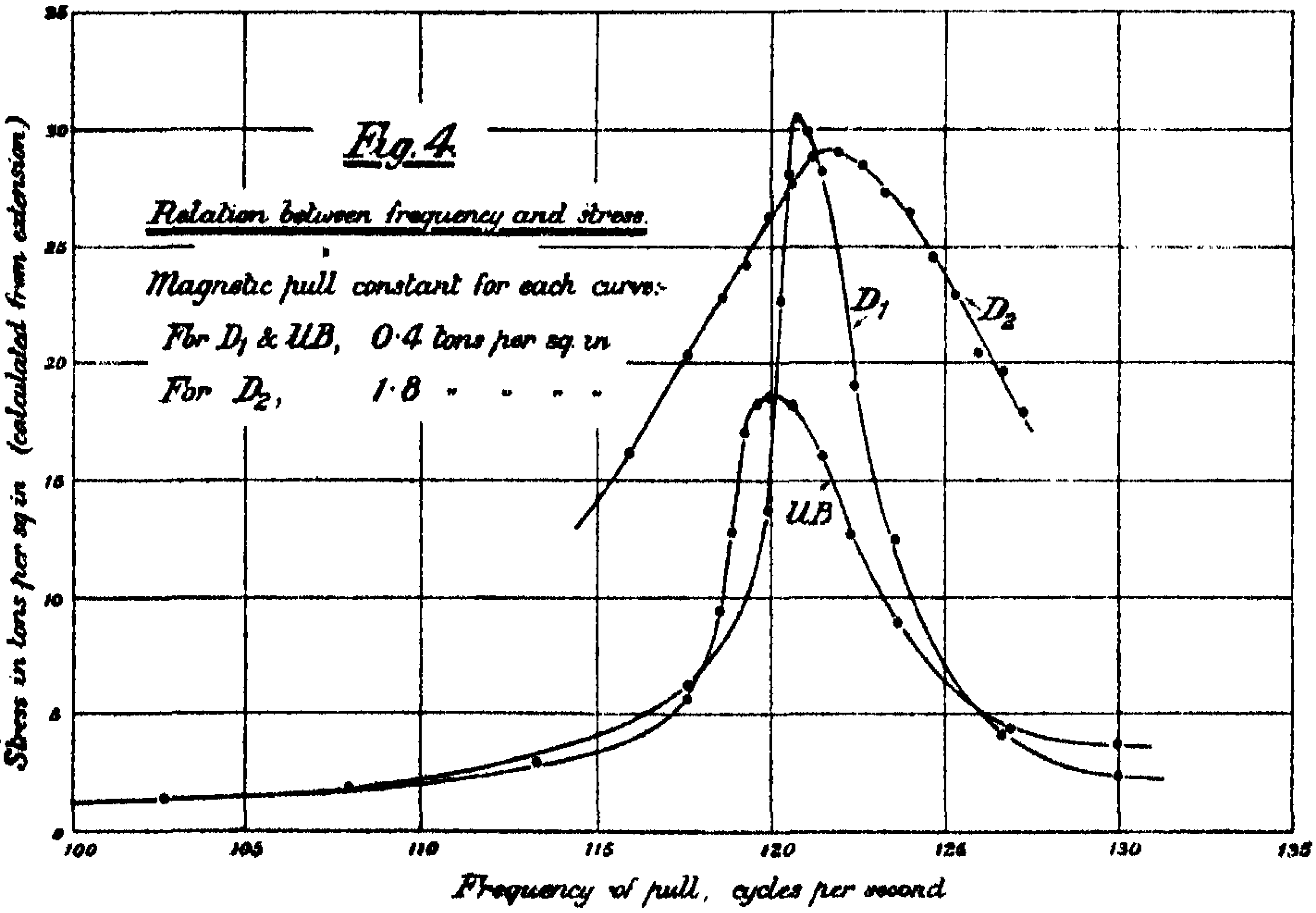


Fig. 4.

Relation between frequency and stress.

the elastic limit. It was observed that much more heat was developed in the bar UB than in D_1 (which was of a different brand of steel), and it is probable that the difference between the two curves is mainly due to this cause. When these trials were made the machine was bolted to a very heavy block of concrete, and it is improbable that much energy was dissipated by vibration. When the third curve (D_2) was taken, the machine had been shifted on to a lighter foundation. The vibration in the surrounding floor was then perceptibly greater, and this is probably the cause of the smaller magnification of pull observed in this case (about 17 times). It will be observed that the resonance point is much less marked, the curve having a flatter maximum. This is in practice an advantage, though more power is taken to drive the machine, because the stress is less affected by slight alterations of speed.

The pull of the magnet varies between zero and a maximum value, and is always such as to give tension in the piece. The mean value of this pull is half the maximum value or range of pull, and (in consequence of the magnification by resonance) is small compared with the total range of stress. Such as it is, it is more or less counteracted by the weight of the mass E, so that in the normal working of the machine the mean stress is almost zero, and the limits of stress are nearly equal in tension and compression. The machine has been used in this way throughout the experiments described in this paper. It is easy to apply any desired steady tension by means of a screw and spring balance (see fig. 2), and thus to alter the ratio of the tension and compression limits.

Measurement of Stress.

As already indicated, the quantity directly measured in this machine is the change of length of the piece in inches. By applying a static pull to the same piece in a testing machine the relation between pull in pounds and extension in inches can be directly determined, and the stress can then be calculated from a measurement of the section of the reduced portion of the bar on the assumption that Young's modulus is the same for the rapid alternating stress as for the steady pull. The experiments of Sears on the longitudinal impact of rods* justify this assumption completely if the stresses are within the elastic limit. In the present instance the stresses may be rather outside that limit, and the fact that fatigue, resulting ultimately in fracture, occurs, shows that at each application there must be a small extra-elastic extension or compression. Bairstow,† measuring the strain in a piece subjected to cycles of stress slowly performed (about two per minute), and rather outside the limiting range, so that fracture would ultimately result, found that the range of strain, which was at first that corresponding elastically to the stress, slowly increased, owing to the formation of a hysteresis loop of the type shown in fig. 5.' It consists of the two parallel elastic portions AB and CD which correspond to the normal Young's modulus of the material and the curved portions BC and DA. The error committed in calculating the stress from the strain on the assumption of perfect elasticity is represented very approximately by LM. After a good many thousand reversals this loop settled down to a constant form which apparently persisted till fracture. The extra-elastic strains at these slow speeds are considerable; for instance, in a steel whose limiting range was probably about ± 13 tons, the application of a range of ± 14 tons gave ultimately a hysteresis loop whose width (LM) was about 1½ tons, or 10 per cent. of the range.

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* 'Camb. Phil. Soc. Proc.,' vol. 14, p. 257.

† 'Phil. Trans.,' A, vol. 210, p. 35.

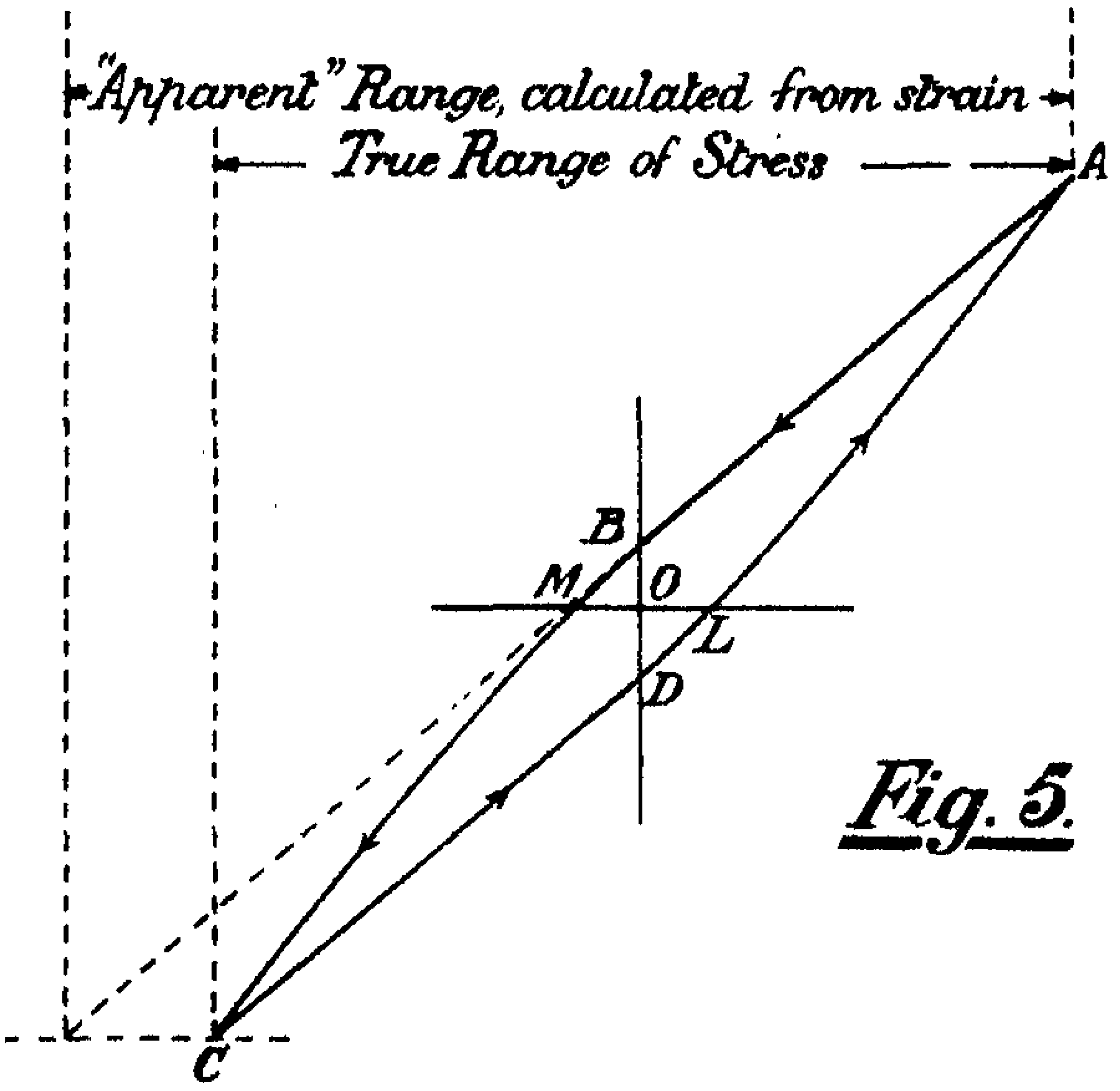

Fig. 5.

It is, however, quite certain that the non-elastic portion of the strain in the high-speed machine is nothing like so great, because, if it were, the magnification of the pull at the resonance point would be much less than is actually found. The magnetic pull, by its action on the moving weight, provides all the energy dissipated mechanically in the system, whether by defective elasticity of the piece, vibrations of the floor, or other causes. The work done per cycle is easily calculated from the range of pull P and the movement of the weight d; it is, in fact, $\frac{1}{4}\pi Pd$ if the frequency corresponds to maximum resonance. This sets an upper limit to the area of the hysteresis loop, and thus to the amount of extra-elastic strain. It is not difficult to show that, even if the whole work done by the magnet is accounted for by hysteresis in the piece, the range of stress differs from the value corresponding to perfect elasticity by an amount not exceeding about 2 P.* For instance, in the curves D_1 and UB (fig. 4), the error in measuring the stress must have been less than 0·8 ton per square inch, and was probably a good deal less. In D_2, which was exactly the same steel as D_1, the magnetic pull is much greater, but this, as has already been explained, is due to the greater vibration of the floor.

These considerations seemed to justify the view that, while the stress calculated from the change of length of the piece in this machine must be rather too high, the error could not be important, so long as the magnetic pull was but a small fraction of the range of stress. It was, however, thought desirable to determine the acceleration of the moving mass, and thus to obtain a direct measurement of the pull exerted by it. For this purpose a needle was fixed horizontally at a convenient point on the mass E, and a microscope, magnifying about 60 diameters, was sighted on the reflection, in the surface of the needle, of an electric lamp. By properly adjusting the position of the lamp, a very sharp line could be obtained, whose position, when the machine was at rest, could be defined within 1/10,000th of an inch. With the machine in action, this line was drawn out vertically into a band, whose length could be measured against a transparent scale in the field of the microscope correct to about 1/5000th of an inch. The microscope was supported for this purpose, with its axis horizontal, on a table loaded with iron plates, and resting on thick blocks of rubber placed on the heavy block of concrete to which the machine was bolted. In this way movement of the microscope itself was completely eliminated, and the apparent movement of the needle in its field corresponded to the actual motion of the weight. The wire guys V, being stretched fairly taut, prevent any angular motion of the weight, so that the movement of its centre of gravity is equal to that of the needle, wherever the latter be attached. The sufficiency of this constraint was proved by attaching a mirror to the weight and observing through a telescope the reflection of a distant lamp filament. Not the slightest tremor could be seen when the supply of current to the machine was suddenly thrown on, though an angular movement, giving a displacement of the needle (relative to the centre of gravity) of 1/5000th of an inch, would certainly have been detected.

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* If d' be the change of length of the piece in a cycle, and P' the amount (LM in fig. 5) by which the apparent stress calculated from the strain exceeds the true stress, the area of the hysteresis loop is greater than $\frac{1}{2}P'd'$. Hence $\frac{1}{4}\pi Pd$ (work done by magnetic pull P per cycle) is greater than $\frac{1}{2}P'd'$. Now in this particular machine d is about $\frac{5}{4}d'$, hence P' must be less than 2 P.

Having thus obtained the range of movement a of the weight, its acceleration f at each end of its travel can be calculated from the formula $f = p^2a$, where $2\pi/p$ is the periodic time of the cycle. It is here assumed that the motion of the weight is simple harmonic. The mechanical conditions of the problem are such as to justify this assumption. We are dealing in effect with a weight attached to a spring, the other end of which is fixed, and this simple system has practically only one degree of freedom, so that its natural small oscillations will be nearly simple harmonic. Further, the wave form of the alternating E.M.F. supplied is nearly simple harmonic, and the corresponding magnetic pull, which depends only on the flux, will be of a similar character, and will force approximately simple harmonic vibrations in the mass of a period equal to its own period. Finally, under normal circumstances, the frequencies are adjusted so that the natural period of the mass is approximately equal to that of the force, and the selective action of resonance has the effect of accentuating that type of motion of the weight whose period corresponds with the fundamental period of the applied force.

A record of the extension of the piece in terms of the time was taken by causing one of the extensometer mirrors to throw a spot of light on to a revolving drum. The curve so traced showed no appreciable departure from a sine wave. It must, however, be remembered that in consequence of the increased importance in the acceleration of high frequency terms in the displacement, a departure from simple harmonic motion which could not be detected on the record might produce a considerable change in the acceleration. The justification of the assumption that for this purpose the motion may be treated as simple harmonic therefore rests mainly on the theoretical considerations mentioned above. The photographic records, however, were useful as showing the very regular character of the cycle of stress produced in the machine.

The forces acting on the weight are the pull in the bar and the pull of the magnet. At the point of resonance these two forces will differ in phase by a quarter of a period, and consequently at the two ends of the travel of the weight, when its acceleration is a maximum, the pull exerted by the magnet will be zero. At these points therefore the mass multiplied by the acceleration is equal to the pull in the rod, and the range of pull in pounds may therefore be taken as equal to $2\,\mathrm{M}ap^2/g$, where $2a$ is the range of movement of the weight observed in the microscope. If the frequency of the magnet pull differs from the natural frequency by such an amount as considerably to reduce the movement of the weight, the magnetic pull comes nearly into phase with the pull in the bar, the relation of signs being such that if the force frequency is the greater the magnetic pull assists the pull in the rod to accelerate the weight, while if the natural frequency be the greater these pulls are in opposite directions. Thus in the first case the range of pull calculated from the movement of the mass should exceed, and in the second should fall short of, that shown by the extensometer by an amount equal to the range of pull exerted by the magnet.

The following table gives one complete set of observations made with the object of comparing the different methods of getting the stress.

The material used in this trial and in the endurance tests described below was a mild steel containing 0·18 per cent. of carbon, with a breaking stress of about 30 tons per square inch.

Frequency of stress cycle, per sec.	100.	100.	116.	120.	134.
Range of extension in piece :—					
Extensometer A (thousandths of an inch)	1·6	2·5	8·6	9·1	0·9
,, B (,, ,,)	1·5	2·5	8·2	8·9	1·1
Microscope A (,, ,,)	1·6	2·5	8·6	9·1	1·0
Mean	1·6	2·5	8·4	9·0	1·0
Stress calculated from extension (tons per sq. in.)	*5·5*	*8·5*	*28·7*	*30·7*	*3·4*
Magnetic Pull :—					
Volts on test-coil (100 turns)	47·5	58·5	46	49	48
Maximum flux density (kilo-lines per sq. cm.)	4·4	5·4	3·6	3·8	3·3
(1) *Range of magnetic pull* (tons per sq. in.)	*1·5*	*2·3*	*1·1*	*1·1*	*0·9*
Acceleration Pull :—					
Movement of mass observed in microscope (thousandths of an inch)	2·4	3·6	12·1	12·7	1·6
(2) *Corresponding range of stress* (tons per sq. in.)	*4·0*	*6·0*	*27·3*	*30·6*	*4·8*
Sum or difference of (1) *and* (2)	*5·5*	*8·3*	(*28·4*)	—	*3·9*
Range of stress calculated from frequency (assuming that resonance occurs at frequency 119)	5·1	7·9	(29·0)	—	3·3

The point of resonance in this case was probably very near 119 periods per second. At 100 periods and at 134 periods the magnetic pull would be very nearly in phase with the pull in the piece. It will be seen that at the first of these frequencies the sum and at the second the difference of the magnetic pull and the acceleration pull agrees closely with the tension in the piece. The frequency of 116 is near to but is certainly below the resonance frequency. There will be a considerable difference of phase in this case, but not so much as 90°. Consequently the stress in the piece should exceed that required to accelerate the weight by something less than the magnetic pull of 1·1 tons per square inch. In fact, it appears to exceed it by 1·4 tons per square inch. At 120 periods we are very close to the resonance point, but probably rather past it. Here the difference of phase will be nearly 90°, and it will be seen that the stress required for acceleration is very near to that calculated from the extension. The last line of the table gives the stress calculated from the magnetic pull P by the formula $P/(1-n^2)$, where n is the ratio of the forced to the free period. This is, of course, not applicable to frequencies near the resonance point, when the amplitude is controlled largely by the dissipative forces, but it gives results in fair agreement with the observations at lower or higher frequencies.

A great number of comparisons of the stress estimated from the acceleration and that estimated from the extension have been made on different pieces of the same steel, at or near the point of resonance, and with a range of stress of 30 to 32 tons per square inch. These observations, taken altogether, reveal a systematic difference between the two; the stress calculated from the extension being higher by perhaps ¾ ton per square inch on the average. It seems probable that this is mainly due to defective elasticity, which becomes apparent in this particular steel when the true stress exceeds 30 tons per square inch. The endurance tests which follow were made on the same steel.

It may be observed here that the phenomenon of increasing hysteresis under the influence of alternating stress which was observed by Bairstow at low speeds is completely reproduced at the high speed of this machine.* If the true stress, as shown by the movement of the weight, be maintained constant at a fairly high value, the strain shown by the extensometer slowly increases, reaching a steady value after the lapse of some thousands of reversals. At the same time the magnetic pull has to be quite noticeably increased in order to maintain the stress. The piece also gets considerably hotter.

Comparison of Endurance at Different Speeds.

Some systematic endurance tests were then carried out on the same steel with the object of finding whether the high speed had any effect on resistance to fatigue. Dr. Glazebrook kindly arranged that a series of trials of the material should be made at the National Physical Laboratory in the direct stress machine designed by Dr. Stanton,† whom I must thank for the great interest he has shown in the tests and the trouble which he has taken in carrying out this part of the work. The steel contains 0·18 per cent. of carbon and 0·7 per cent. manganese and was supplied in the form of bright drawn bars of 1 inch or 1¼ inch diameter. The cold drawing to which these bars are subjected has the effect of raising the elastic limit of the bar as a whole, but that this change is not serious is apparent from the tensile tests given below, and anyhow it is of little consequence in a comparative trial. Three bars of this steel in all were used in the test, two being of 1 inch in diameter, and the other (D) 1¼ inch. These bars are referred to as C, D, and E respectively. Tensile tests were made on two specimens cut from bar D with the following average results:—

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* Bairstow, 'Phil. Trans.,' A, vol. 210, p. 42. The increase of hysteresis under alternating stress has also been observed by Turner, who noticed the rise of temperature of a tube subjected to a Wöhler test, 'Engineering,' Sept. 4, 1911.

† Stanton and Bairstow, 'Inst. Civ. Eng. Proc.,' vol. 166, p. 78. The first machine on these lines was made by Messrs. Reynolds and Smith (see 'Phil. Trans.,' A, vol. 199, p. 265).

Elastic limit in tension	19·3 tons per sq. in.
„ compression	13·4 „
Maximum stress	29·5 „
Elongation on 8 in.	16 per cent.
Reduction in area.......................	60 „

For the tension test the bar was turned down to a diameter of ¾ inch, and for the compression to 1 inch. The elastic limits correspond to the load at which permanent set first becomes distinctly apparent in a Ewing extensometer; that for compression is not well defined. A series of seven pieces cut from bar C and tested in the direct stress machine at the National Physical Laboratory gave the following results, which have been plotted in fig. 1:—

N.P.L. No. of specimen.	Mark.	Reversals per minute.	Range of stress, in tons per sq. in.	Reversals to fracture.	Total duration of test (hours).
216	C VI	1351	38·8	6,613	0·08
217	C IV	1351	34·9	7,633	0·09
220	C V	1246	29·65	44,244	0·59
219	C I	1104	26·45	197,761	3·0
218	C III	1063	17·7	1,017,337*	15·9
218	C III	1283	25·7	150,981	1·96
221	C II	1092	22·8	1,113,484*	17·2
221	C II	1125	25·5	1,003,610*	14·9
225	C VII	1076	24·6	326,550	5·0

* Unbroken.

Pieces of another bar (D) of the same material were tested in the direct-stress reciprocating machine and also in a high-speed Wöhler machine with the following results:—

N.P.L. No. of specimen.	Mark.	Reversals per minute.	Range of stress, in tons per sq. in.	Reversals to fracture.	Total duration of test (hours).
		Direct Stress Machine.			
222	D I	1084	27·7	120,000	1·8
223	D II	1084	27·7	119,200	1·8
224	D J	1084	24·6	326,560	5·0
		Wöhler Machine.			
77	D J	2200	27·0	1,637,500	12·5
105	D J	2200	25·5	7,000,000*	53·0

* Unbroken.

The endurance tests on the new high-speed machine were carried out on pieces of the same bars. It may be noted that the diameter of the test-piece—¼ inch—is the same as that of the piece used in the direct stress machine at the National Physical Laboratory, so that exactly the same portion of the bar was tested. The trials were not all continuous, but were split up into periods separated by intervals of rest ranging from a few minutes to several hours. But most of the continuous runs covered at least a million cycles, and if a piece was not broken in one day, the trial was usually continued on the next, and so on, until fracture occurred. In all the trials the piece got perceptibly warm, and if it reached a temperature (judged by the hand) of 60° or 70° C. at the centre, a jacket of blotting paper was applied and kept soaked with water. It does not appear that the rise of temperature materially affected the endurance, for the pieces seemed to break indifferently at the centre or near the ends, where of course the temperature was by conduction kept nearly atmospheric.

Continuous observation was kept of the extensometer reading during a trial. After the first few minutes this settled down to a constant value, and very little adjustment was then required. The "apparent stress" given in the second column of the following tables is that calculated from the extension on the assumption of perfect elasticity.

In the first series of trials, which were made on the "C" bar the strain was kept at rather a high value, and there must have been considerable departure from elasticity. The true stress is, therefore, uncertain except in the one case C_7 where the movement of the mass was measured. Continuous observation was, however, kept of the E.M.F. on the test-coil and as pointed out in the last section the "apparent stress" cannot exceed the true stress by more than twice the range of magnetic pull calculated from these observations. This is the basis of the assertion (in cases other than C_7) that the stress in the following series of trials never fell short of 30 tons per square inch.

No. of bar.	Range of stress (tons per sq. in.).		Time (hours).	Millions of reversals to fracture.	Remarks.
	By extensometer (apparent).	True stress.			
C_3	32—34	Exceeded 30	15	6·0	Four periods.
C_5	34—35	Exceeded 30	15½	6·2	Three periods, one of 12 hrs. continuous.
C_6	33—34	Exceeded 30	29	11·5	Four periods, one of 14 hrs.
C_7	31—33	30—32 (by movement of mass)	7	2·8	Three periods.
C_8	32—33	Exceeded 30	8¼	3·4	Two periods.

In most of these tests the piece heated to such an extent that it was necessary to jacket it with wet blotting paper.

Further trials were made in two pieces cut from another bar of the same material (D). Piece D_1 was the same as that used in the comparisons of different methods of getting the stress which have been described above, in the course of which the stress varied, rising sometimes to 31 tons per square inch. On the conclusion of these experiments it was put through a steady endurance test at an "apparent" range of stress of 30·5 tons per square inch, calculated from extensometer. It broke after 10 million cycles taking about five periods of five hours each on consecutive days (total, 25 hours). As the piece kept cool (it was not necessary to jacket it) it may be inferred that the elasticity was nearly perfect to the end of the test, and that the estimate of stress derived from the extensometer was not far wrong. Allowing liberally for all possible errors, it may be asserted that the stress exceeded 29 tons per square inch throughout this test. The treatment of piece D_2 was as follows:—

Range of stress (tons per sq. in.).		Total time (hours).	Total reversals (millions).	Remarks.
By extensometer.	By acceleration.			
28·2	26·8	32	12·8	Four periods, about 8 hrs. each.
		Four weeks' rest.		
29·0	28·8	15	6·0	Three periods, about 5 hrs. each.
		Two days' rest.		
30·0	28·2	14	5·6	Three periods, one of 12 hrs. continuous.
31·0	30·0	15·8	6·3	The piece was perceptibly hotter.
32·0	29·0	5·0	2·0	Two periods. Broke.

Until the last period of five hours the piece was only slightly warm, and the elasticity must have been nearly perfect. During the last period it got very hot, and had to be jacketed. It is probable that the stress did not fall short of 29 tons during the last 50 hours and 20 million reversals—certain that it did not fall short of 28 tons.

Finally, a piece E_1, cut from another bar of the same material, was subjected to the following treatment:—

Range of stress (tons per sq. in.).		Total time (hours).	Reversals (millions).
By extensometer.	By acceleration.		
31	Not less than 30	6·7	2·7
32	Not less than 31	2·5	1·0 (broke)

Each of the runs was continuous, and they took place on successive days. In each continuous observation was kept of the movement of the weight, and care was taken that the true stress (calculated from the movement) should never fall short of 30 tons and 31 tons per square inch respectively.

Reference to the curve (fig. 1) on which the observations with the slow-speed machine (1100 revolutions per minute) are plotted, shows that the probable life of this material under a range of 28 tons per square inch at that speed is about 100,000 reversals and one and a-half hours of time; and with a range of 30 tons about half as much. In the Wöhler machine (at 2000 revolutions per minute) the endurance is apparently a little greater, but neither the number of observations nor the amount of the difference is sufficient ground on which to base an inference as to the effect of speed. But at the higher speed of 7000 alternations per minute the evidence seems to be conclusive that the endurance is greater. Not only is the number of reversals of a given range of stress required to break the piece greatly increased, but the actual time during which it must be subjected to alternating stresses is also increased. It is not, however, proved that the limiting range of stress, namely, the maximum range which will not cause breakdown however often it be repeated, is greater at the higher speed. Though the observations suggest that conclusion, it is quite possible that sufficiently prolonged vibration at a range of stress of 27 tons per square inch would ultimately have ruptured the material. Since, however, it takes 10 million reversals and some 25 hours of time to break the piece with a range which certainly exceeds 29 tons, it would appear probable that the number of reversals and the time required with a range of 27 tons would be very great indeed, perhaps so great that for practical purposes the piece might be regarded as unbreakable by this load if it be applied and removed sufficiently rapidly.

Probable Causes of Speed-effect.

In the hysteresis loop (fig. 5) into which the stress-strain curve of a metal undergoing fatigue apparently always develops, the straight portions AB and CD correspond to perfect elasticity, but during the curved parts BC and DA the material is flowing or taking permanent set. There seems to be little doubt that fatigue is the cumulative effect of the internal slips which accompany this flow, and that the rate of fatigue is determined mainly by the amount of the extra-elastic strain occurring in a cycle (BD in fig. 5) which Bairstow has called the "cyclical permanent set." Accepting that view, there are two ways in which speed may be expected to affect endurance. First, if the speed be high enough there may not be time for the full amount of flow corresponding to BC and DA to take place at each reversal. The amount of flow, and therefore of damage to the material, occurring at each cycle will then be reduced. So far as this factor is concerned, therefore, increased speed will make for greater endurance, provided that the speed is sufficient materially to affect the stress-strain relation. Second, there is the phenomenon of recovery. Any over-strained material tends to recover its elasticity with time. This tendency must be supposed to be continually at work during the progress of a fatigue test, repairing the ravages of the successive over-strains. Obviously, so far as it goes, its operation will be relatively more effective at slow speeds. Hence the effect of this second factor is to associate greater endurance with slower speed, and is opposite to that of the first. The combined effect of the two would be to cause the endurance (always reckoned as the number of stress-cycles to fracture) to diminish at first as the speed is increased, then to reach a minimum value and increase again. But if the influence of recovery on the progress of a continuous fatigue test is small, then the minimum of the curve connecting speed and endurance becomes very flat and we shall get approximately constant endurance until the speed reaches a certain limit, after which the endurance increases.

The conclusion expressed in the last sentence is in accord with the facts, and the inference that recovery is not an important factor is at least probable. It may be, however, that the opposed actions of recovery and of time-change in the stress-strain relation happen to cancel each other pretty accurately over the flat part of the curve. Finally, to settle the point it would be necessary to carry out comparative tests in which the speed is the same but the rate of recovery different. The most obvious way would be to try the effect upon endurance of raising the temperature of the piece, which is known to accelerate recovery. Such an experiment would give very useful information. As pointed out above, there is some evidence in the experiments with the high-speed machine that the rate of fatigue, at that speed at any rate, is not much affected by temperature; but the observations were not directed especially to this point, and the evidence is not conclusive.*

The direct determination of the other factor—the effect of speed on extra-elastic stress-strain relations—also requires much more experimental study than it has yet received. It is certain, however, that if the cycle of stress be completed in 1/100 second or less, the effect must be large. The greater endurance at high speeds found in the present research is perhaps sufficient evidence for this assertion, but there is independent confirmation of it in the results of experiments which have been made on the extension of a wire under the action of a blow.† The wire (stretched vertically) was stressed by the blow of a weight falling against a stop at its lower end. Measurement of the momentary extension, and calculation from the mass of the weight and the height of fall, alike showed that the average stress over the top 20 inches of the wire must have reached a maximum value exceeding by 50 per cent. the static elastic limit, and sufficient if long continued to break the wire. Yet it was found that 11 such blows in succession extended the part of the wire under measurement by less than 1/2000 part of its length, and the wire was almost perfectly elastic up to the maximum stress applied by the blow. The stress was outside the elastic limit for about 1/1000 second at each blow, which is of the same order as the time during which the over-stress lasts in each cycle in the high-speed machine.

The arguments here used would lead to the conclusion that though the rate of fatigue under the action of stress which ultimately ruptures the piece will be lower at high speeds of reversal, yet the limiting range of stress which the piece will sustain indefinitely without breaking will be independent of speed. For if a single reversal produces any permanent effect whatever it is to be expected that a sufficient number must ultimately fracture the piece, and it is difficult to believe that time can be a factor determining whether or no such permanent effect shall exist, though it may affect its amount. It is quite possible, however, that as the time occupied by each cycle is diminished the effect produced may diminish in greater proportion. And the ultimate result may be that for practical purposes the limiting range is raised on account of the great length of time required to cause fracture. Further, it is noted that when the rate of fatigue is very slow the property of recovery becomes relatively more important, and it is at least conceivable that it may be more than competent to overcome the fatigue altogether and so really raise the limiting range.

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* Some experiments on the effect of temperature on fatigue have been made by Unwin, who found that the endurance of mild steel was slightly increased at a temperature of about 200° C., 'Inst. Civ. Eng. Proc.,' vol. 166, p. 117.

† Hopkinson, 'Roy. Soc. Proc.,' vol. 74, p. 498.

The observations described in this paper were for the most part taken and reduced by my assistant, Mr. H. Quinney, whom I must thank for the zeal and ability with which he has carried out the work. I wish also to acknowledge valuable assistance given at various stages by Mr. C. Trevor-Williams, advanced student in the University of Cambridge, and by my brother, Mr. R. C. Hopkinson, Trinity College.

The Mechanism of the Semi-permeable Membrane, and a New Method of Determining Osmotic Pressure.

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Introduction.

For the theoretic exposition of osmotic pressure, no further attention need be paid to the membrane than to postulate its semi-permeability. It is, however, desirable that the physical properties of the membrane should not be lost sight of, especially from the experimental point of view.

Leaving out of account for the moment the mechanical requirements of a rigid membrane, let us imagine a system in which we have a solution separated from the pure solvent by a thick layer of another liquid which can take up or dissolve the solvent, but not the solute.

Such a system might be sufficiently realised by means of an aqueous solution of cane sugar, ether, and water, since sugar is insoluble in ether, while ether dissolves a small quantity of water. Both water and sugar solution take up some ether, but that is of no immediate interest in the present considerations. This complication will be, however, dealt with later on. If it is desired to imagine the necessities of gravity complied with, the sugar solution and the water can be supposed to be placed side by side in a vessel and kept from mixing by an impervious vertical partition reaching to a certain height; then ether poured in, so as to cover all and to act the part of a semi-permeable membrane separating the solution from the water.

Ether takes up about 1·05 per cent. of water when placed in contact with it, but takes up less than this from sugar solution, the amount depending upon the concentration of the solution. For equilibrium at the water-ether surface the ether must thus contain 1·05 per cent. of water, while at the solution-ether surface a less quantity is necessary for equilibrium to exist there. Diffusion through the ether prevents this equilibrium existing, so that water will pass across from the water side to the solution side.*

If the ether could rigidly maintain its position so as to prevent the volume of the solution increasing, the hydrostatic pressure of the solution would go up owing to water passing into it. This process, we must suppose, would, under such circumstances, come to an end when, owing to the increase of pressure, the amount of water taken up by the ether from the sugar solution reached the amount taken up from water at the ordinary pressure.

A practical equivalent to the assumed rigidity might be provided in our supposed experiment by having the level on the solution side lower than on the water side, the difference in levels depending upon the strength of the solution used. By making the column of ether sufficiently high, the necessary pressure could obviously always be provided to enable the amount of water held by the ether at the solution-ether surface to equal that held near the water-ether surface.

The pressure competent to bring about this state of equilibrium in the ether would thus appear, from the above considerations, to be the osmotic pressure of the sugar solution.

The complication above alluded to, arising from the solution of our "membrane" in both the solution and solvent, introduces probably only an apparent and not a real difficulty, and is met, it would seem, in the case of sugar solution, ether, and water, by the amount of ether held by the solution when under the equilibrium or osmotic pressure being equal in amount to that held by water at the normal pressure. It is well known that the presence of a salt in water causes a reduction in the amount of ether taken up when ether is placed in contact with the solution, but this amount rises with the pressure. No accurate quantitative determinations have been obtained as to the amount of this, but some qualitative observations bear out the above assumption, in which case the solvent would simply be a solution of ether-water instead of pure water.

We could under these circumstances infer that in order to determine the osmotic pressure of a given solution it is only necessary to find the pressure to which a suitable liquid, say ether, must be subjected when in contact with the solution, in order that the liquid may take up as much water from the solution as the liquid takes up from water at the ordinary pressure.

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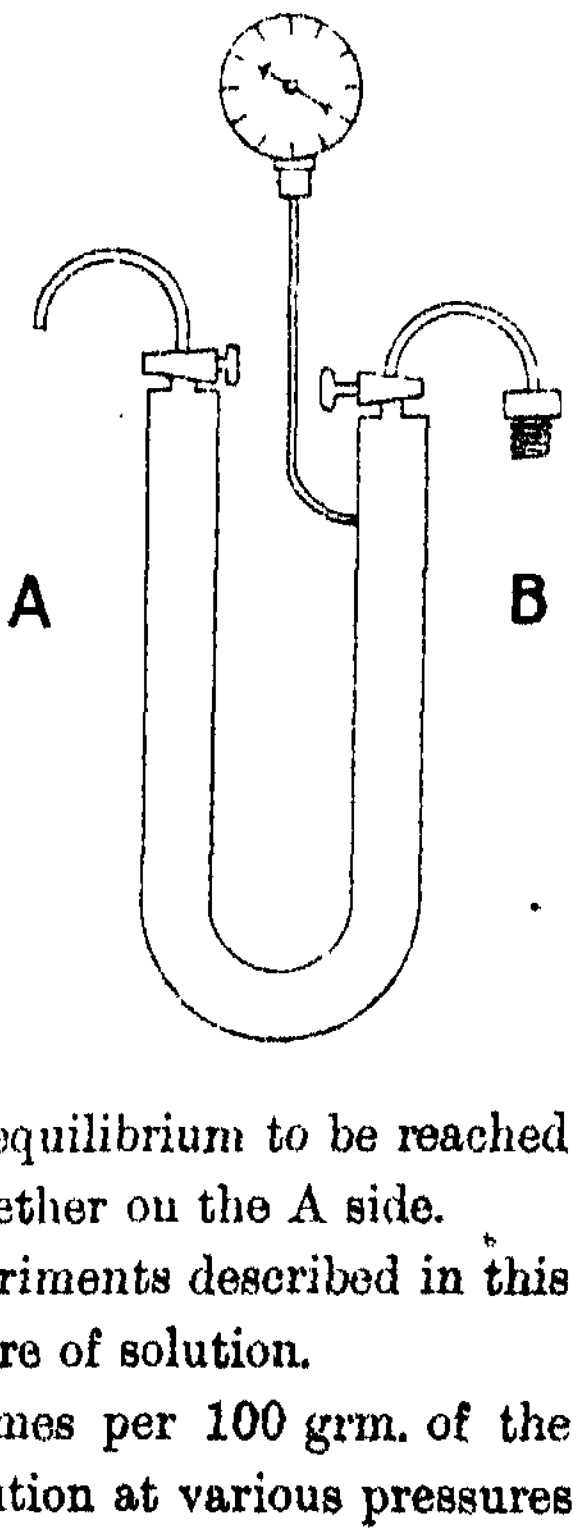
* A small correction may be required to allow for the equilibrium distribution of concentration depending upon the gradient of pressure in the ether.

Method of Experiment.

In order to determine osmotic pressures on this principle an apparatus was constructed in which the solution in contact with ether, or other suitable liquid, could be subjected to hydrostatic pressure of any desired amount. It consisted of a copper U-tube strong enough to stand high pressures, and closed by taps on each side. A gauge was attached for reading the pressures. In this apparatus any pressure up to somewhere over a hundred atmospheres could be obtained.



To charge the apparatus: first, enough solution is introduced to half fill the tube. Then ether is sucked in on the side marked A and the tap closed. By means of a screw coupling B connection is made with a pressure pump and air forced in till the requisite pressure is indicated on the attached gauge when the tap B is closed.

After sufficient time has elapsed for the ether to take up its full complement of water from the solution, the tap A is opened, when the compressed air in the other limb drives the ether out, which is collected and its water content determined. By shaking the tube the length of time required for equilibrium to be reached can be reduced, but care must be taken to keep the ether on the A side.

The strength of the solution with which the experiments described in this paper were carried out was 600 grm. of sugar per litre of solution.

The curve shows the amount of water, in grammes per 100 grm. of the examined ether, found to be taken up from this solution at various pressures ranging from atmospheric up to over 100 atmospheres. It was found in this way that at about 79 atmospheres the amount of water taken up from this strength solution had risen to the amount taken up by ether from water at 1 atmosphere. This amount is indicated on the diagram by the dotted horizontal line. This, according to the above considerations, should be the osmotic pressure of solutions of the particular molecular strength used.

This result may be compared with Lord Berkeley's and Mr. Hartley's* determinations of osmotic pressure made with a semi-permeable membrane of ferrocyanide of copper on porcelain. They plot a curve from their results obtained with cane sugar, from which we can scale off the value of the osmotic pressure for a solution of 600 grm. per litre. This is about 81 atmospheres, and is, within the limits of error, practically the same as the value given by the ether experiments.

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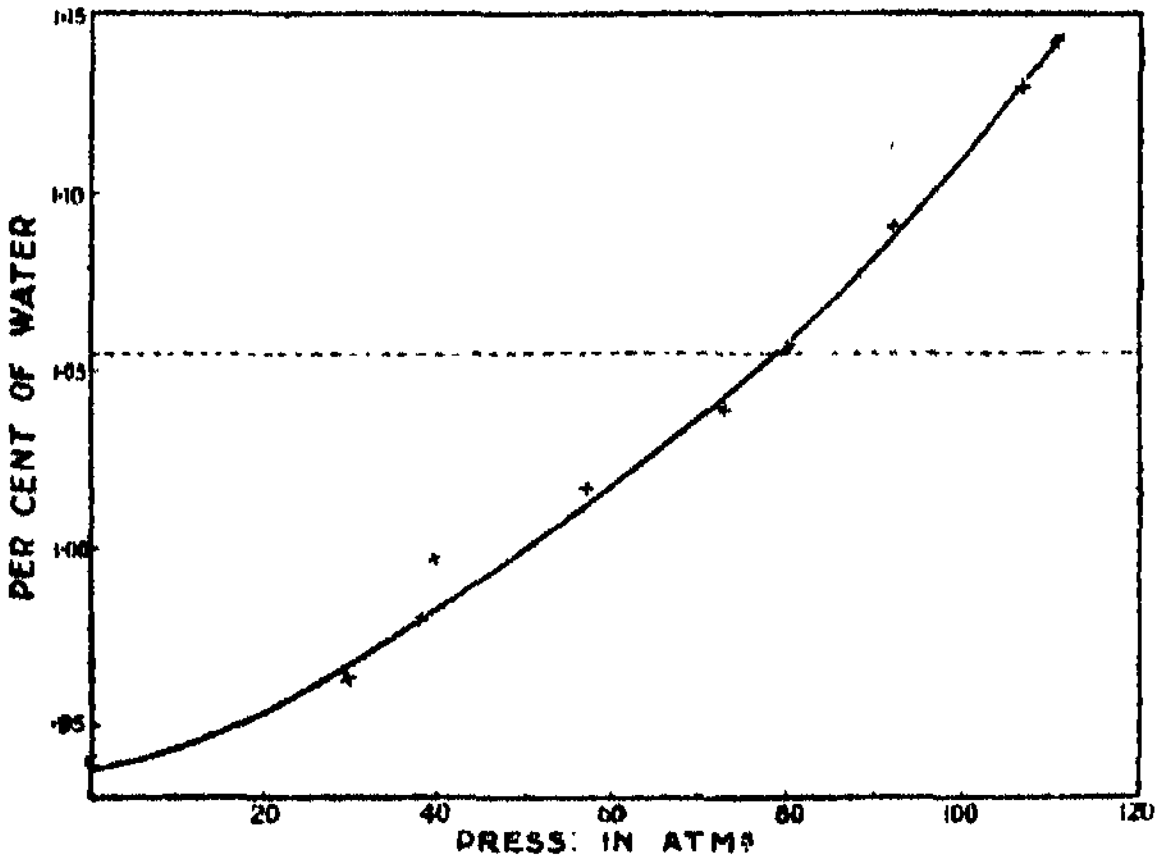
* 'Phil. Trans.,' A, vol. 206, p. 481.



After trying various plans, the one finally adopted for determining the amount of water taken up by the ether was to pass the ether in the form of vapour through calcium chloride drying tubes. The ether was slowly evaporated in a flask placed in warm water. The vapour was led through several drying tubes so as to secure that all the water was absorbed. The escaping ether could be collected and saved when so desired. The drying tubes were kept at 40° C. by placing them in a bath at that temperature. This was sufficiently warm to prevent ether condensing in the tubes, and yet was found not to be too high for substantially absorbing all the water. Before weighing the tubes dry air was run through them, in order to sweep out all ether vapour.

The following table gives the data from which the curve has been plotted. The second column gives the weight of water held by 100 grm. of the ether-water solution in equilibrium with the sugar solution at the corresponding pressure. The corrected weights given in the last column were calculated for convenience of plotting the curve by grouping the observations. This was done for the pressures given in the third column by taking the tangents found from a preliminary curve as giving the rate of change of the weight with pressure, and then taking the mean of the weights so found.

Table I.

Pressure in atmospheres.	Weight held by 100 grm.	Pressure.	Corrected weight.
1	0·935		
1	0·953		
1	0·941		
1	0·938		
1	0·926	1	0·939
30	0·965		
30	0·973		
30	0·953		
30	0·948		
30	0·974	30	0·962
38·1	0·979	38·1	0·979
40	0·964		
40	0·997		
40	0·997	40	0·986
57	1·007		
56·5	1·024		
57·1	1·015		
57·8	1·002		
57·8	1·035	57	1·016
73·1	1·040		
73·5	1·056		
72·8	1·028	73	1·039
80	1·047		
81·5	1·056		
78·9	1·053	80	1·051
93·9	1·103		
92·5	1·093		
92·5	1·089		
92·5	1·098		
91·8	1·077	92	1·090
107·5	1·130	107·5	1·130
110·5	1·143	110·5	1·143

The value assumed for the weight of water taken up by ether at atmospheric pressure when in contact with water is the mean of the following 10 experiments:—

Table II.

1·060	1·032	1·054	1·045	**Mean** 1·0545
1·040	1·052	1·087		
1·048	1·063	1·064		

In the determination of osmotic pressure by the semi-permeable membrane method, the difficulty of finding a suitable membrane for most salts becomes very great when high pressures are resorted to, so that it has been found practicable to work with only a limited range of substances. The method here described opens up a wider field, for less exacting conditions have to be complied with in the working material selected, namely, that it should be a substance which takes up the solvent but does not take up the solute, while, in the case of the material needed for making a semi-permeable membrane, in addition to taking up the solvent but not the solute, it must be either rigid itself or be capable of being mounted on a rigid support.

These determinations were carried out by my assistant, Mr. Burgess, for whose care and accuracy I wish here to acknowledge my thanks.

Mobility of the Positive and Negative Ions in Gases at High Pressures.

By Alois F. Kovarik, Ph.D., John Harling Research Fellow in Physics, The Victoria University of Manchester.

(Communicated by Prof. E. Rutherford, F.R.S. Received November 14, 1911,—Read January 11, 1912.)

Introduction and Purpose.

The velocity of ions in gases at reduced pressures was first investigated by Rutherford[*] and by Langevin.[†] Recently the author and others have carried out similar investigations. The results of these investigations show that for the negative ions in air the product of the mobility and the pressure is constant for pressures ranging from 760 mm. to 200 mm. of mercury, but with further reduction the product increases with the reduction of pressure, this increase becoming very great at low pressures.[‡] For the positive ions in air the product of the mobility and pressure is constant for pressures investigated between 760 mm. and 3 mm. of mercury.[§] Similar results were obtained for the mobilities of the ions in other gases. The results show that if the ion is an aggregation of molecules, this aggregation becomes, at low pressures, less complex in the case of the negative ion, while in the case of the positive ion it persists down to 3 mm. of mercury.

The purpose of the present research was the study of the mobilities of both kinds of ions in gases at high pressures. The method of investigation is based on the mathematical expression, developed by Prof. Rutherford,[||] for the current between two plates, assuming that a very intense ionisation exists near the surface of one of the electrodes.

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[*] Rutherford, E., 'Camb. Phil. Soc. Proc.,' 1898, vol. 9, p. 401.

[†] Langevin, N. P., 'Ann. de Chim. et de Phys.,' 1903, vol. 28, p. 289.

[‡] Kovarik, Alois F., 'Phys. Rev.,' 1910, vol. 30 (4), p. 415.

[§] Todd, G. W., 'Camb. Phil. Soc. Proc.,' 1910, vol. 16, p. 21.

[||] Rutherford, E., 'Phil. Mag.,' 1901, vol. 2, p. 210.

The expression developed is

$$i = 9V^2K/32\pi d^3.$$

where i is the current per square centimetre through the gas, K the mobility of the ions, V the potential difference, and d the distance between the plates.

Rutherford* verified this equation experimentally, using for the intense surface ionisation, ionisation produced by a heated platinum plate. C. D. Child,† who developed the same equation independently, utilised it for the measurement of the velocity of ions drawn from flame gases.

In the present work this equation was again tested experimentally, and was utilised for the purpose of measuring the mobility of the ions in gases at high pressures. The intense surface ionisation was obtained by using a preparation of ionium‡ at one of the plates and reducing the range of the α-particles by using the gas at high pressures. Since ionium is separated with thorium, some β- and γ-rays due to thorium were present. With the specimen used this volume ionisation was not found to be of importance. If β-rays are present in abundance, their volume ionisation superposed on the surface ionisation due to α-particles at high pressure is very noticeable, as was found in an experiment where freshly prepared polonium was used, the polonium containing a considerable amount of radium E, which emits β-rays.

Apparatus.

The apparatus used was a cylinder 8 cm. in diameter and 12 cm. deep, made especially for high pressure work, and shown in fig. 1. The upper electrode in most of the experiments was 1·054 cm. in radius, and was encircled by a guard ring. The insulation was amber. The lower electrode was held in position by ebonite fastened at the bottom of the cylinder, and was connected with the battery. The gas passed into the cylinder through a valve at the lower part of the cylinder, and its pressure was measured by an attached calibrated gauge.

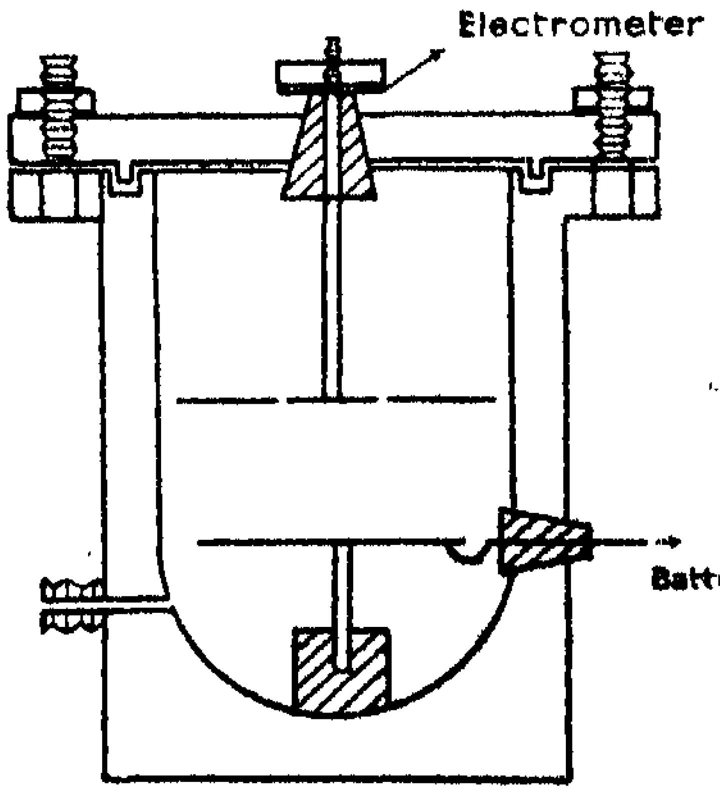

Fig. 1.

The ionium was spread as a very thin layer over a plate 6 cm. in diameter, and this plate served as the lower electrode. In order to protect the ionium from sudden gusts of gas, a cylinder of ebonite was placed round the wall inside the cylinder. By means of keys the lower plate could be brought to a positive or negative potential. An electrometer with condensers of suitable capacities was used to measure the current between the electrodes.

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* Rutherford, E., 'Phys. Rev.,' 1901, vol. 13 (6), p. 321.

† Child, C. D., 'Phys. Rev.,' 1901, vol. 12 (3), p. 137.

‡ This material was part of the ionium separated by Prof. Boltwood from the radioactive residues loaned by the Royal Society to Prof. Rutherford ('Roy. Soc. Proc.,' 1911, A, vol. 85, p. 77).

Test of the Equation.

Experiments were first carried out to test the equation. In order to find out if the equation is applicable to the present problem, it was necessary to show :—

(1) That the current varies as the square of the potential difference. (2) That the current varies inversely as the cube of the distance. (3) That the ionisation produced by the α-particles of the ionium used was sufficiently great, so that any increase in the ionisation had no effect on the current for a given potential difference and a given distance.

These experiments were carried out in air. The air was first compressed into a large cylinder to 120 atmospheres by means of a liquid air compressor. The amount of moisture present at this pressure must be small. From this cylinder it was passed very slowly into the apparatus so as not to scatter the active material. When a desired pressure was reached it was necessary to wait some time before taking measurements on account of the motion and the changing temperature of the gas.

The method of taking readings was to measure the time of deflection of the spot of light over a definite calibrated portion of a scale. This was done for both positive and negative currents for every potential. Readings for a given potential difference were taken often in each set and were used as a check.

Table I gives the results of an experiment when the pressure of the air was 59·5 atmospheres, and the distance between the plates was 2·81 cm. The potential difference is given in volts and the current per centimetre in E.S.U. These results are shown graphically in fig. 2. If the currents are plotted against the square of the potential difference, a straight line passing through the origin is obtained for the first 80 volts. Above 80 volts, there is a deviation from the square of the potential difference law. The range of voltage for which the current is proportional to the square of the potential difference varies for different pressures and also for different distances, being greater for higher pressures and greater for greater distances. It is within this range of potential difference, where the law holds, that the current must be determined for the calculation of the mobility of the ions. This was done in all cases by obtaining a set of readings similar to those of Table I, plotting the currents against the square of the potential difference and then selecting some convenient value for the potential difference and measuring the value of the current on the graph.

Table I.—Air.

Pressure = 59·5 atmospheres. d = 2·81 cm. T = 19° C.

P.D., in volts.	Square of P.D.	Current in E.S.U. per cm.^{2}.	
		Positive.	Negative.
6	36	$2 \cdot 3 \times 10^{-5}$	$1 \cdot 48 \times 10^{-5}$
10	100	3·8	4·98
14	196	7·0	9·4
20	400	13·0	18·2
26	676	20·6	32·0
32	1024	32·6	46·5
41	1681	49·5	68·6
51	2601	77·2	108
61	3721	112	161
71	5041	142	206
82	6724	187	263
123		356	410
164		509	564
205		630	646
287		748	807
492		966	1040

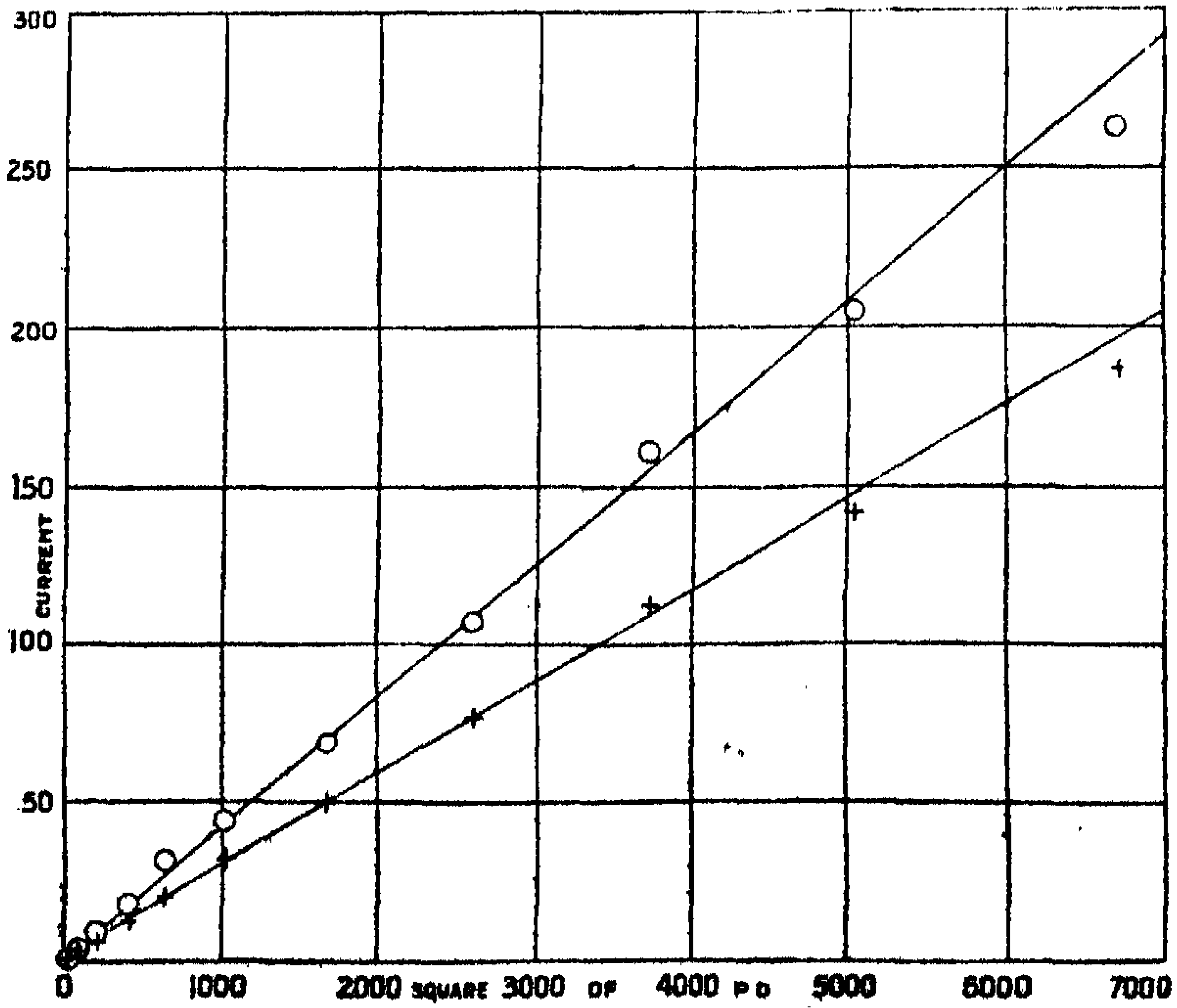

Fig. 2.

In testing the equation for distance, measurements were made for current for a potential difference of 30 volts for different distances. The pressures were all above 30 atmospheres, and the current, which, as will be seen, varies inversely with the pressure (in air), was reduced to the value for the mean pressure of all the experiments, viz., 50 atmospheres. The product of the current per square centimetre thus obtained and the cube of the distance between the plates is given in Table II for the various distances used.

Table II.—Various Distances between Electrodes.

Air at 50 atmospheres. P.D. = 30 volts = 0·1 E.S.U. T = 19° C.

Distance, in cm.	d^3.	$i \times d^3$. i in E.S.U. per cm.^{2}; d in cm.	
		Positive.	Negative.
0·805	0·52	$8·3 \times 10^{-3}$	$10·4 \times 10^{-3}$
1·36	2·52	7·4	9·7
1·53	3·58	7·6	10·2
1·76	5·45	7·7	10·3
2·31	12·33	7·6	10·1
2·81	22·2	7·3	10·2
3·27	35·0	7·0	9·3
3·78	54·0	7·2	9·4
4·27	77·8	6·8	8·9

It will be noticed that the values of this product are reasonably constant although the cube of the distance changed in the ratio of 1 to 150. With the greater distances, the values are somewhat lower, due, no doubt, to the fact that the field became less uniform. On the whole, however, the results may be considered fairly satisfactory in proving that, for the distances used, the current varies inversely as the cube of the distance between the plates.

After a series of experiments the amount of ionium was considerably increased, the layer still being extremely thin. The current for a definite potential difference and distance between the plates, and for a definite pressure, did not change, which shows that the surface ionisation was intense enough, and that the current was independent of further increase in the intensity of the ionisation.

Experiments with Air.

In the experiments to determine the mobility of the ions at various pressures, care had to be taken in the choice of the distance between the plates for the following reasons: At lower pressures the range of the α-particle becomes greater and the correction for this range becomes appreciable for small distances. The correction for the range of the α-particles consisted in decreasing the distance between the electrodes by one half of the range at the particular pressure used. With great distances between the plates the field could not be made uniform on account of the small dimensions of the apparatus. With distances between 2 and 3 cm., however, the field appeared to be quite uniform and the correction for the range was small for the high pressures.

The results obtained for the various pressures in air are given in Table III. The actual mobilities in centimetres per second per volt per centimetre for the two kinds of ions, as deduced from Rutherford's equation, are given, and also the products of the mobility and the pressure in atmospheres. It will be noticed from the results that the velocity varies inversely with the pressure up to 75 atmospheres. The mean values for the product of the mobility and pressure in atmospheres for pressures above 30 atmospheres at a temperature of 19° C. are 1·89 and 1·346 for the negative and the positive ions respectively, with a ratio of 1·405. The values obtained by Zeleny* at atmospheric pressure, and at a temperature of 13·5° C., are respectively 1·87 and 1·36, giving a ratio of 1·375.

Table III.—Air. Mobility at various Pressures.

$d = 2·81$ cm. T = 19° C.

Pressure, in atmospheres.	Mobility, in cm./sec. per volt/cm.		Mobility × Pressure.		Ratio of mobilities.
	Positive.	*Negative.*	*Positive.*	*Negative.*	
74·6	0·0187	0·0262	1·39	1·96	1·41
70·6	0·0192	0·0270	1·36	1·91	1·40
59·5	0·0226	0·0318	1·34	1·89	1·41
58·0	0·0258	0·0366	1·37	1·94	1·41
50·6	0·0261	0·0366	1·32	1·85	1·40
47·6	0·0272	0·0392	1·30	1·86	1·43
41·7	0·0317	0·0449	1·32	1·87	1·42
36·8	0·0378	0·0506	1·37	1·87	1·37
31·2	0·0433	0·0600	1·35	1·87	1·39
21·1	0·0615	0·0830	1·30	1·75	1·35
13·8	0·103	0·138	1·37	1·84	1·40
		Mean.........	1·346	1·89	1·405

Experiments with Carbon Dioxide.

In these experiments a cylinder of carbon dioxide was used. The gas was found to be saturated with moisture, and to contain about 0·3 per cent. of air, a trace of HCl, and a slight trace of alcohol. On letting the gas into the apparatus, the insulation generally broke down. Attempts were made to dry the gas partially by placing calcium chloride into the apparatus and letting the apparatus stand for a day. The insulation never broke down in this case, and the negative ions were found to have a greater velocity than the positive ions, but consistent results could not be obtained for some reason. As arrangements were not made to dry the gas previous to passing it into the apparatus, the only results included are those for the moist gas. These results are given in Table IV. It will be noticed that the product of the mobility and the pressure is practically constant up to a pressure of 40 atmospheres, but that it decreases considerably as the gas approaches the liquid state. The mobility of the positive ions in moist carbon dioxide is greater than the mobility of the negative ions, as was also observed by Zeleny and others, the ratio of mobilities being 0·95 for pressures up to 40 atmospheres and unity for pressures above 50 atmospheres. The mean values of the product of the mobility and pressure in atmospheres taken for pressures up to 40 atmospheres and 19° C. are 0·705 and 0·67 for the positive and negative ions respectively. Zeleny's values at atmospheric pressure and 17° C. are 0·82 and 0·75 respectively, giving a ratio of 0·92.

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* Zeleny, J., 'Phil. Trans.,' 1900, A, vol. 195, p. 193.

Table IV.—Carbon Dioxide (moist). Mobility at various Pressures.

$d = 2·31$ cm. T = 19° C.

Pressure, in atmospheres.	Mobility in cm./sec. per volt/cm.		Mobility × Pressure.		Ratio of mobilities.
	Positive.	Negative.	Positive.	Negative.	
57·0	0·0091	0·0091	0·52	0·52	1·00
52·4	0·0116	0·0116	0·61	0·61	1·00
46·7	0·0137	0·0136	0·64	0·63	0·98
41·8	0·0160	0·0148	0·67	0·62	0·93
36·7	0·0187	0·0181	0·69	0·66	0·96
31·5	0·0234	0·0225	0·74	0·71	0·96
26·0	0·0264	0·0254	0·69	0·66	0·96
21·1	0·0355	0·0340	0·75	0·72	0·95
15·3	0·0465	0·0427	0·71	0·65	0·92
10·2	0·0732	0·0679	0·75	0·69	0·93
Mean for values for pressure up to 40 atmos. …			0·705	0·67	0·94

Experiments with Hydrogen.

The hydrogen used in these experiments contained 0·7 per cent. nitrogen and very little moisture (about 0·02 per cent.). The range of the α-particles in hydrogen is four times that in air, consequently greater pressures were necessary to realise the condition of surface ionisation. The results of the experiments are given in Table V. It will be noticed that the mobility varies inversely as the pressure up to 72·5 atmospheres—the highest pressure used in the experiments. The mean values of the product of the mobility and pressure in atmospheres at 20° C. are 8·19 and 6·20 for the negative and the positive ions respectively, giving a ratio of mobilities equal to 1·32. The mobilities for the negative and positive ions in hydrogen at atmospheric pressure and 20° C., as found by Zeleny, are 7·95 and 6·70 respectively, giving a ratio of mobilities equal to 1·19.

Table V.—Hydrogen. Mobility at various Pressures.

$d = 2·31$ cm. $T = 20°$ C.

Pressure, in atmospheres.	Mobility, in cm./sec. per volt/cm.		Mobility × Pressure.		Ratio of mobilities.
	Positive.	Negative.	Positive.	Negative.	
72·5	0·084	0·110	6·10	8·00	1·31
68·4	0·090	0·120	6·15	8·25	1·34
62·7	0·096	0·126	6·01	7·90	1·31
58·1	0·105	0·139	6·10	8·08	1·32
52·8	0·116	0·153	6·14	8·10	1·32
47·3	0·132	0·175	6·25	8·29	1·32
41·9	0·146	0·198	6·11	8·30	1·36
36·7	0·170	0·228	6·25	8·38	1·34
31·5	0·201	0·267	6·34	8·41	1·33
25·7	0·248	0·322	6·38	8·28	1·30
20·8	0·305	0·388	6·35	8·08	1·27
		Mean.........	6·20	8·19	1·32

Summary.

The mobilities of the positive and negative ions in dry air, dry hydrogen, and moist carbon dioxide were measured. The method of measurements is based on Rutherford's equation for the velocity of ions between two plates, the assumption in the theory being that a strong surface ionisation exists at one of the plates. This assumption was satisfied experimentally by using the α-particles from ionium as the ionising agent, and reducing their range by using the gases at high pressure. The equation was tested experimentally.

The results for the mobilities of the ions in these gases are as follows: In dry air and dry hydrogen the mobility varies inversely as the pressure up to 75 atmospheres, the highest pressure used. In moist carbon dioxide the product of the mobility and pressure is constant for pressures up to

40 atmospheres, but for higher pressures the product decreases as the gas approaches the liquid state.

The mean values for the products of the mobility and pressure in atmospheres, for the range of pressures for which the product was constant, are, for the negative and positive ions respectively, in dry air, 1·89 and 1·346; in dry hydrogen 8·19 and 6·20, and moist carbon dioxide 0·67 and 0·705 cm. per second for a potential gradient of 1 volt per centimetre.

In conclusion, I take great pleasure in expressing my best thanks to Prof. Rutherford for suggesting this research, and for the valuable advice given by him during the progress of the experiments.

On the Viscosities of Gaseous Chlorine and Bromine.

By A. O. Rankine, D.Sc., Assistant in the Department of Physics, University College, London.

(Communicated by Prof. F. T. Trouton, F.R.S. Received November 22, 1911,—Read January 25, 1912.)

Introduction.

The object of the experiments about to be described was to determine the viscosities, at various temperatures, of gaseous chlorine, bromine, and iodine, by comparison with air. The apparatus, however, proved unsuitable in several respects for working at the higher temperatures required. It has, nevertheless, yielded satisfactory results at the lower temperatures; and the viscosity of chlorine at atmospheric temperature and at 100° C., and that of bromine at the latter temperature only, have been measured by means of it. These values are now published, pending the extension of the investigation on the lines indicated, with a new form of apparatus which promises to be entirely adequate for the purpose.

The chief difficulty which presents itself in working with the halogen gases is the readiness with which they attack mercury. On this account, the method I have previously used* for viscosity determinations was rendered unsuitable; but it has been found possible to retain one of its most desirable features, viz., the mercury pellet, which serves the double purpose of creating a constant pressure difference, and of measuring the volume of gas emerging from the capillary. In other respects the apparatus is quite different, the main object in its construction being to prevent contamination of the mercury. This has been sufficiently secured by causing the pellet to aspirate the gas through the capillary tube, with a deep layer of air acting as a kind of buffer between them. The failure of the method at high temperatures was chiefly due to the mercury pellet becoming unstable, owing to the diminution of surface tension.

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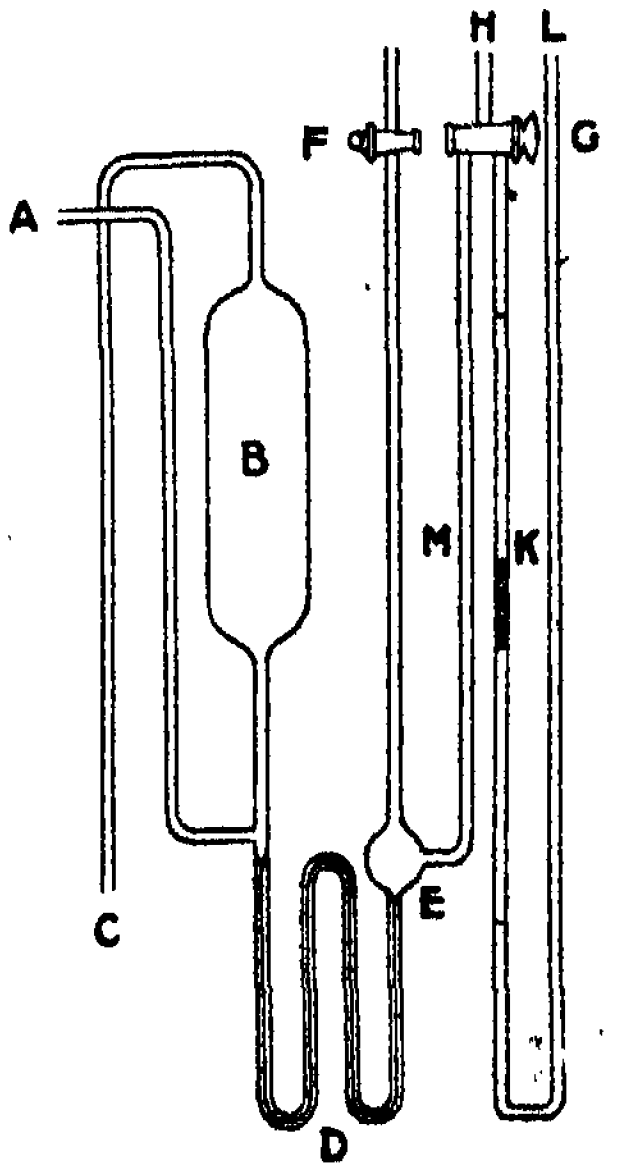
* 'Roy. Soc. Proc.,' A, vol. 83, pp. 265 and 516.

Apparatus and Experimental Method.

The principle of the method will be gathered from fig. 1, which represents the apparatus in semi-diagrammatic form. Only the essential features are shown. B is a bulb of about 100 c.c. capacity, which could be filled with the gas under test. The capillary tube D consists of rather more than a metre of fine-bore tubing, the internal diameter of which is about 0·2 mm. This is bent, as shown, in order to save space, and the exit leads into a small bulb E, which is of sufficient capacity to contain easily the gas drawn through the capillary during one determination. The tube in which the mercury pellet moves is marked K in the diagram. By means of the tap G it may be connected with E through the tube M; and, under these circumstances, the pellet creates a constant pressure difference between the two ends of the capillary; for the end L is open to the atmosphere, as also is C. The volume of gas sucked through the capillary is indicated by the distance moved through by the pellet. Thus we may obtain an approximate measure of the ratio of the viscosities of two gases by comparing the times of fall of the mercury pellet between two fixed marks on the tube K, when the two gases, in turn, occupy the bulb B and the tubes leading to it. In the present apparatus the bore of the tube K is about 3 mm. in diameter, the length of the pellet about 9 cm., and the volume of gas drawn through the capillary in one determination is about 4 c.c. This gas, on emerging, occupies the bulb E, and, except by diffusion through the long tube M, does not reach the mercury pellet. By this means it is possible to avoid contamination of the mercury, or, at any rate, to delay it sufficiently for a series of consistent measurements to be made.

Figure I.



In order to repeat the experiment two things are necessary: the mercury pellet must be raised, and the gas in E must be replaced by air. These are done in the following way:—The end H is connected to a large reservoir of air, the pressure of which is kept below that of the atmosphere by an amount slightly exceeding the pressure arising from the mercury pellet. The tap G can be used to connect the tube K with H, and the pellet is then sucked to the top of the tube. Connection between M and H can also be secured by means of G, and then by opening the tap F dry air may be drawn through E so as to displace the gas it contains. The tap F is then closed, but before connecting M and K, M is connected with H in order to avoid the large immediate fall of the mercury pellet which would otherwise take place, owing to the expansion of the air in E and M.

It was at first expected that the great density of chlorine and bromine might be relied on to prevent considerable mixture through convection and diffusion of air into B through C, which, as before stated, was open to the atmosphere. This, indeed, turns out to be the case with bromine. But preliminary experiments with carbon dioxide showed that it would be better to allow the gas to overflow slowly throughout the series of measurements, and this has therefore been done.

Further, the exit C was arranged at the same level as E, so as to practically eliminate the small hydrostatic pressure arising from the gas itself. The pressure difference was therefore in all cases the same, viz., that determined by the mercury pellet. The whole apparatus, with the exception of the tubes A, C, and L, and the taps G and F, was immersed in suitable baths, first in a water reservoir at atmospheric temperature, and afterwards in a double-walled steam jacket.

In each case the viscosity has been compared with that of air under exactly similar conditions, the values obtained being

$$\eta_{\mathrm{Cl}}/\eta_{\mathrm{air}} \text{ at } 12{\cdot}7^\circ \text{ C.}, \quad \eta_{\mathrm{Cl}}/\eta_{\mathrm{air}} \text{ at } 99{\cdot}1^\circ \text{ C.}, \text{ and } \eta_{\mathrm{Br}}/\eta_{\mathrm{air}} \text{ at } 98{\cdot}7^\circ \text{ C.}$$

The chlorine was prepared by the addition of pure hydrochloric acid to potassium permanganate, the gas then being washed, dried, and condensed in a bulb immersed in alcohol cooled by solid carbon dioxide. It was then allowed to evaporate slowly and entered the apparatus by way of a glass spiral which was kept at the temperature required for the particular experiment. This secured that the gas used had the proper temperature.

The bromine used was of the purest quality obtainable from Kahlbaum. It was mixed with phosphorus anhydride and thence distilled directly into the apparatus. The gas under these circumstances entered at the temperature of boiling bromine (about 60° C.), and did not attain the required temperature (100° C.) so long as the flow continued. Hence the observed times of fall of the mercury pellet during this stage were lower than those obtained after evaporation had ceased, when the gas really assumed the temperature of the bath. A considerable number of minutes elapsed before a further and progressive increase in the times of fall ensued, owing to the slow diffusion of air into the bulb B. The values used in the determination were therefore those following the complete evaporation of the bromine and previous to the increase due to diffusion of the air.

Results.

The following determination is given in detail to illustrate the probable accuracy of the method and the mode of treatment of the observations.

September 27, 1911. Barometer, 76·50 cm. Temperature, 99·1° C.

	Times of fall in seconds.	
	Air.	Chlorine.
	200·2	155·6
	199·8	154·6
	199·6	154·6
	200·2	154·6
	199·6	154·2
	199·4	155·0
		154·4
Mean	199·8	154·7

The approximate value of the ratio η_{Cl}/η_{air} at 99·1° C. is therefore 154·7/199·8 = 0·7743.

This has to be corrected for the difference of slipping coefficients of chlorine and air. The method of doing this has been previously described,* and need not be repeated here.

The corrected value is

$$(\eta_{Cl}/\eta_{air})_{99 \cdot 1} = 0 \cdot 772.$$

The value of η_{air} at 99·1° C. found by the author† is $2 \cdot 186 \times 10^{-4}$ C.G.S.

Hence at 99·1° C. $\eta_{Cl} = 1 \cdot 688 \times 10^{-4}$ C.G.S.

The other value for chlorine obtained is that at 12·7° C. At this temperature

$$(\eta_{Cl}/\eta_{air})_{12 \cdot 7} = 0 \cdot 726.$$

At 12·7° C. $\eta_{air} = 1 \cdot 786 \times 10^{-4}$ C.G.S. Hence

$$\eta_{Cl} = 1 \cdot 297 \times 10^{-4} \text{ C.G.S.}$$

In the case of bromine

$$(\eta_{Br}/\eta_{air})_{98 \cdot 7} = 0 \cdot 8557.$$

At 98·7° C. $\eta_{air} = 2 \cdot 184 \times 10^{-4}$ C.G.S.

Hence $\eta_{Br} = 1 \cdot 869 \times 10^{-4}$ „

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* 'Roy. Soc. Proc.,' A, vol. 83, pp. 517 and 518.

† 'Roy. Soc. Proc.,' A, vol. 84, p. 191.

The collected values are given below:—

Gas.	Temperature.	$\eta \times 10^4$ C.G.S.
Chlorine	12·7° C.	1·297
Chlorine	99·1°	1·688
Bromine..................	98·7°	1·869

Assuming that Sutherland's law holds for chlorine over this temperature range, we may calculate the value of the constant C in the equation

$$\eta = \mathrm{K}\frac{\mathrm{T}^{\frac{1}{2}}}{1+\mathrm{C}/\mathrm{T}},$$

which may be put in the more convenient form

$$\frac{\eta_2}{\eta_1} = \left(\frac{\mathrm{T}_2}{\mathrm{T}_1}\right)^{\frac{3}{2}}\left(\frac{\mathrm{C}+\mathrm{T}_1}{\mathrm{C}+\mathrm{T}_2}\right).$$

From the values given above,

$$\eta_{99\cdot1}/\eta_{12\cdot7} = 1\cdot302,$$

and the value thus obtained for C is 325.

It should be pointed out, however, that this may have a very considerable error, owing to its sensitiveness to variation in the ratio $\eta_{99\cdot1}/\eta_{12\cdot7}$. If we suppose that this ratio is subject to an error of ½ per cent. (and this represents approximately the order of accuracy of the measurements), C will have a value lying between 305 and 352. Thus the value given may be 9 per cent. from the true value, and a more reliable estimate cannot be made until the measurements are extended to higher temperatures.

Discussion of Results.

It is interesting to observe the bearing of these results upon the two laws with reference to viscosity to which the author has previously called attention. These may be stated as follows:—

(i) For most of the gases for which data are available Sutherland's constant is proportional to the critical temperature, or

$$\mathrm{T}_c/\mathrm{C} = \text{constant} = 1\cdot14.$$

(ii) *For the group of inert gases the square of the viscosity at the critical temperature is proportional to the atomic weight, or*

$$\eta_c^2/\mathrm{A} = \text{constant} = 3\cdot93\times10^{-10}.$$

The first of these laws may be tested with respect to chlorine. The critical temperature of this gas is in the neighbourhood of 416° absolute. For chlorine, therefore,

$$\mathrm{T}_c/\mathrm{C} = 416/325 = 1\cdot28,$$

a number which is considerably in excess of the value for other gases. It should be noticed, however, that the possible error in C referred to above is quite sufficient to account for the divergence.

The second law cannot be tested directly, for the variation with temperature of the viscosity of bromine is not known. If, however, we calculate the viscosities of chlorine and bromine at *corresponding* temperatures, *i.e.* temperatures which bear equal ratios to the respective critical temperatures, we find that a similar rule applies in this case also.

The critical temperature of bromine is 575° absolute. The temperature at which the viscosity of bromine is known is 371·7° absolute, or 0·6466 of the critical temperature. The corresponding temperature for chlorine is $416 \times 0{\cdot}6466 = 269°$ absolute. The viscosity of chlorine at this temperature may be found by extrapolating over the small range of 17° C., since the viscosity at 12·7° C. or 285·7° absolute is known. The results are as follows:—

Temperature $= 0{\cdot}6466\ \mathrm{T}_c$.

Gas.	$\eta \times 10^4$.	A.	η^2/A.
Chlorine	1·218	35·5	$4{\cdot}19 \times 10^{-10}$
Bromine	1·869	80·0	$4{\cdot}37 \times 10^{-10}$

The two numbers in the last column differ by only 4 per cent., notwithstanding the fact that any error in η has been doubled by the process of squaring. This constancy at least suggests that for the halogen group of gases η_c^2/A is probably also constant, although not the same constant as for the inert gases. Indeed, it may be shown that if for a group of gases the two laws referred to above hold, it follows that at all corresponding temperatures η^2/A is constant.

Let θ denote the ratio T/T_c. Then Sutherland's formula assumes the form

$$\frac{\eta}{\eta_c} = \theta^{\frac{3}{2}}\left\{\frac{\mathrm{C}/\mathrm{T}_c+1}{\mathrm{C}/\mathrm{T}_c+\theta}\right\}.$$

Now, if $\mathrm{C}/\mathrm{T}_c =$ constant (as is the case for the majority of gases), it follows that for equal values of θ

$$\eta/\eta_c = \text{constant}.$$

Hence, if η_c^2/A is constant, η^2/A at corresponding temperatures is necessarily also constant. The latter rule has been shown to hold in the case of chlorine and bromine at one pair of corresponding temperatures only, and although this does not prove that a similar rule holds at the critical temperatures, the probability is that the extension of the investigation will show this to be the case.

On the Relation between Current, Voltage, Pressure, and the Length of the Dark Space in Different Gases.

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(Communicated by Sir J. J. Thomson, F.R.S. Received December 7, 1911,—Read January 25, 1912.)

In a previous communication by one of us[*] the results of a number of experiments on the relation between current, voltage, pressure, and the length of the dark space were given for the gases hydrogen, nitrogen, oxygen, and air. The first part of the present paper consists of a continuation of that communication giving the results obtained with carbon monoxide, argon, and helium, together with some constants for these and the gases previously mentioned which were not published at the time.

The second part deals with a systematic investigation of the behaviour of the inactive gases when in a state of great purity.

Part I.—For detailed description of the apparatus and method employed the reader is referred to the above-mentioned paper. It will be sufficient to state here that the discharge took place between aluminium discs, 10 cm. in diameter and about 17 cm. apart, the cathode being of the guard-ring type to ensure accurate measurements of the current density.

The case of *carbon monoxide* is particularly interesting as it is the only compound gas yet experimented on which allows the passage of a continuous current without very serious decomposition. In its behaviour it resembles exactly the active elementary gases. Its dark space is sharp and well defined, but if the current density is increased beyond a certain limit (about half the maximum used for the other gases), the discharge strikes back behind the cathode, and consequently the values of constants obtained are not very accurate.

The *argon* used was certainly impure, for it showed no signs of the primary dark space* exhibited by the pure specimen used in the later experiments. The *helium* also probably contained sufficient impurity to make it behave more or less the same as the active gases and obey approximately the two empirical equations

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[*] F. W. A., 'Roy. Soc. Proc.,' A, 1907, vol. 79, p. 80.

$$D = \frac{A}{P} + \frac{B}{\sqrt{C}}, \quad V = E + \frac{F\sqrt{C}}{P}.$$

Table I gives the values obtained for the constants A, B, E, and F, and for the expression CPD^3/V^2;† D, the Crookes dark space, is measured in centimetres; P, the pressure, in hundredths of a millimetre of mercury; C, the current density, in tenths of a milliampère per square centimetre of the cathode. In the sixth column are given the values of the pressure P_1 at which the dark space is 1 cm. with unit current density, and in the seventh the voltage V_1 between the electrodes under these conditions.

Table I.

	A.	B.	E.	$F \times 10^{-8}$.	$CPD^3 10^5/V^2$.	P_1.	V_1.
Hydrogen	26·5	0·43	144	57·3	57·5	46·8	266
Helium	36	0·49	255*	100	38·8	70·6	395
Carbon monoxide ...	10	0·42	255	41·5	5·75	17·5	489
Nitrogen..............	6·8	0·40	230	28·6	5·75	11·3	484
Air	6·5	0·42	255	23·0	5·70	11·3	457
Oxygen	5·7	0·49	290	17·6	5·55	11·4	444
Argon	5·4	0·34	240*	29·4	2·37	8·2	594

* The high values given here should not be compared directly with the values of E in Table II, as they are obtained by extrapolation of a different part of the curve.

Part II.—The general method of conducting the experiments was the same as before, but some different measuring instruments were used.

The discharge tube was of the same type, being a large cylindrical bottle 12 cm. in diameter, provided with a plane glass window at one side for observing the dark space. The anode and cathode were parallel aluminium discs 9 cm. apart, closely fitting the tube, the latter being of the guard-ring type previously described. The area of the centre portion was 6·90 cm.

The length of the dark space was measured by a sighting arrangement similar to that used in the former experiments.

The potential fall across the tube was determined by means of a Weston voltmeter.

The pressure of the gas was measured by means of a McLeod gauge constructed with tubing 2·5 mm. in diameter in order to minimise the effects of capillarity. It was usually cut off from the discharge tube by a tap to prevent access of mercury vapour, but the two vessels were always allowed to remain in communication for three or four minutes before measuring the pressure. In making a series of experiments the gas was always admitted at the highest pressure required. The pressure was then reduced by means of a Töpler pump. The ratio of the volume of gas removed at each stroke to that of the whole apparatus was determined, sufficient time being allowed for equilibrium to be established, and this afforded a means of checking the pressure given by the gauge. The two values were found to be in good agreement.

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* F. W. A., 'Roy. Soc. Proc.,' A, 1907, vol. 80, p. 45.

† *Loc. cit.*, also F. W. A., 'Roy. Soc. Proc.,' A, 1911, vol. 84, p. 526.

The current was obtained from a battery of 500 small lead accumulators, and passed through two large water resistances in parallel. Before taking a reading it was adjusted to a fixed value by means of a null method, the connections of which may be seen from the annexed diagram.

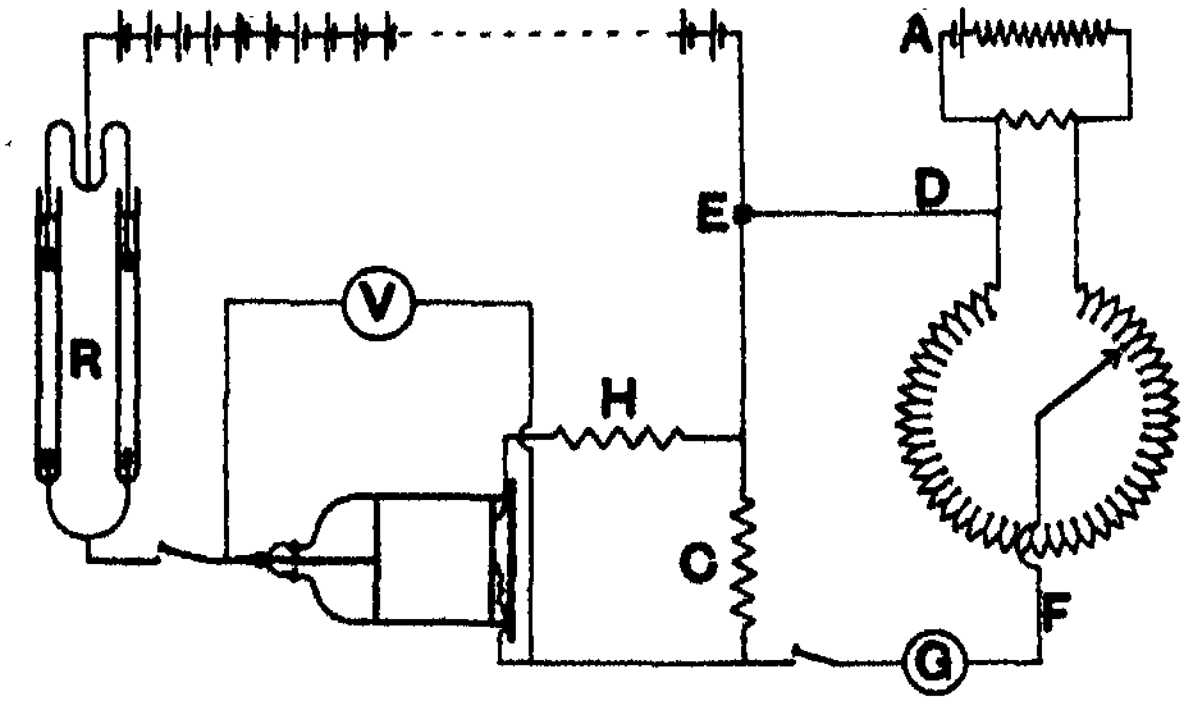

Fig. 1.

The current from an accumulator A passes through two resistances of 200 Ω and 5 Ω in series. In parallel with the latter is connected a current divider consisting of 100 20 Ω coils in series, and a sliding contact connecting with the terminals of any coil. In this way the potential difference between the wires D and F could be set at 101 different voltages, rising by equal increments from 0 to about 1/20 volt. The main current through the centre portion of the cathode of the discharge tube passed through a 50 Ω shunt C to earth.

In making a measurement, the sliding contact of the current divider was moved to a fixed point, and the liquid resistances R adjusted until the potential difference across the shunt C exactly balanced that between D and F, the galvanometer G being used to indicate the equilibrium point. The apparatus was calibrated by passing known currents and simultaneously measuring the E.M.F. of the accumulator A. Since the current necessary to produce equilibrium is proportional to this E.M.F. the voltage of A was tested from day to day, although it remained very constant. The maximum current measured was very nearly 1 milliampère, corresponding to 100 coils of the current divider between D and F, and the other fixed currents adopted corresponded to 81 coils, 64, 49, 36, 25, 16, 9, 4, and sometimes 1, these values being chosen because the square roots and inverse square roots of the current were the functions considered.

An adjustable resistance H was inserted between the guard ring of the cathode and the earth connection, for by varying this until the difference in potential between the two parts of the cathode (indicated by a galvanometer not shown in the diagram) was zero, the ratio of the currents through the two portions could be determined. The extreme variation of this ratio was about 15 per cent., and considering the small size of the centre portion of the cathode, it seems probable that the current density over its surface was uniform within the limits of experimental error.

Before starting the experiments the discharge tube was repeatedly filled with oxygen at low pressure and a current passed, the tube being evacuated with charcoal in liquid air, as soon as the yellow colour of the oxygen turned grey from contamination by carbon compounds. After 10 days the rate of production of the latter gases became very slow, and experiments were then started with the inactive gases.

After a few preliminary difficulties had been overcome, it was seen that these gases were very similar to one another in their manner of conducting the discharge, but at the same time they differed considerably from the active gases, in that the two equations given on p. 169 did not hold with any degree of accuracy. The first of them, connecting the length of the dark space with the current density, was true for high current densities, but the second, connecting voltage and current density, seemed to be in no way applicable. If, however, P be eliminated from the equations, the result is $V-G = KD\sqrt{C}$ where $G = E-BF/A$ and $K = F/A$, and this relation was found to agree remarkably well with the experimental results.

One noticeable feature is common to the gases of the helium group, this being that they all exhibit the primary dark space close to the cathode discovered by one of us in helium and hydrogen.* In argon and krypton it is not very obvious, but in the other three gases it is exceedingly striking, especially at low current densities. The conditions of experiment were, unfortunately, not suitable for accurate measurements of the very small length *d* of this dark space, but from some rough results obtained, the values of the expression dV/D, which appeared to be fairly constant, were found to be approximately 10 volts for neon, 12 for argon, 15 for krypton, and 20 for xenon, the figures previously obtained for hydrogen and helium being 10 and 20 respectively.

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* F. W. A., 'Roy. Soc. Proc.,' A, 1907, vol. 80, p. 45.

Neon was the first gas investigated. It had been prepared originally by fractionation from a mixture with helium, and was repurified by means of charcoal in liquid air before use. Two samples were examined, one of which probably contained a little helium, but no difference could be detected between them.

The boundary of the dark space was not as sharp as in oxygen, especially at low current densities, and its position was rather difficult to determine owing to the large amount of light in the dark space itself. The colour of the latter was rather redder than that of the negative glow, which was orange, but there was no obvious spectroscopic difference.

The first experiments made appeared to indicate that the above-mentioned equations held good in the case of neon as well as for the active gases, but after about 20 series of readings at various pressures it was found that the relation between V and $\sqrt{C}$ at constant pressure tended to deviate from the linear type and become hyperbolic, the curve rising fairly steeply at first,

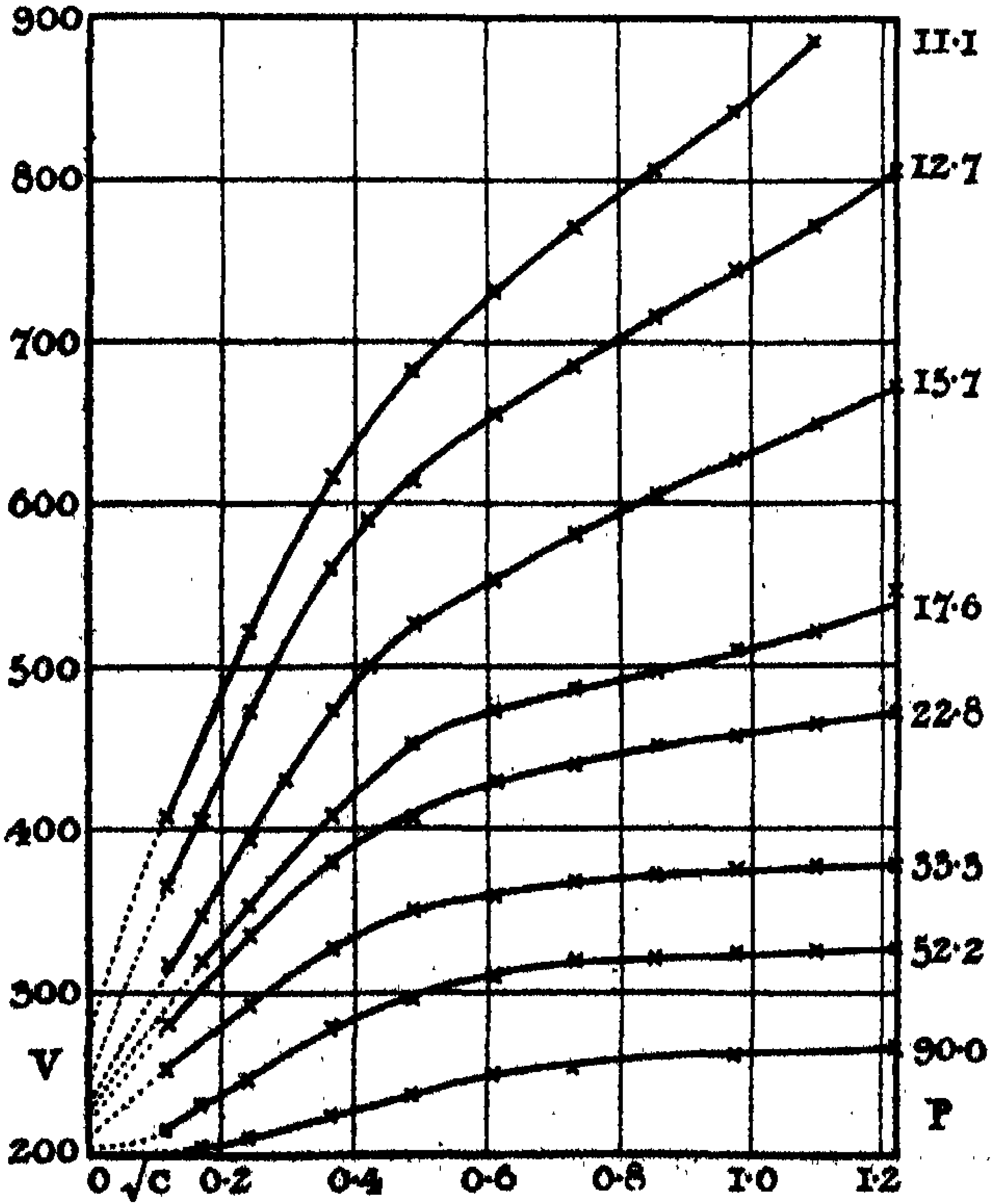

Fig. 2.—Neon—Relation between Current and Voltage.

and then turning over and becoming nearly horizontal. After continuing the experiments for some time, fresh gas being used for each series, the bend in the curve became much sharper, but finally a constant state was reached. Some of these curves are shown in fig. 2. The lowest one and the fourth from the top were obtained with one sample of gas and the rest with the same after undergoing another fractionation to remove possible traces of helium. Several weeks elapsed between the two series of experiments, and other gases were introduced into the discharge tube in the interval.

It will be observed that there is a slight tendency for the curves to bend upwards at high current densities, especially at low pressure. This appears to be a real effect, but at the same time it is very difficult to keep the current constant under these conditions, and the rise in voltage may be exaggerated.

With regard to the shape of the curves at low current densities it is possible that the limiting voltage for zero current is the same for all pressures, but the curves hardly bear extrapolation to one point, and at low pressures the truth cannot be ascertained by means of the apparatus used, because if the current is reduced below a certain limit, the discharge suddenly ceases to pass. At high pressures, however, the curves tend to become horizontal with small currents and the limiting voltage is that which persists when the current is insufficient to cover the cathode.

For the sake of uniformity, all measurements were made as the currents were increased. If the reverse procedure was followed, the voltages obtained were a few volts lower. This is probably due to a combination of effects, such as the presence of mercury vapour, and tiring of the electrodes, which cannot be investigated conveniently in a tube of large dimensions. It seems likely, however, that the real voltages at high current densities are slightly higher than those given. This applies also to the other gases.

With regard to the relation between dark space and current density, the equation $D = A/P + B/\sqrt{C}$ appeared to hold for high current densities, but at low ones D was much smaller than the calculated value. Moreover in the measurements with diatomic gases, B was found to be very constant, while in the case of neon it varied more than in any other gas, being 0·41 at high pressures and 0·81 at low ones. Fig. 3 shows some typical curves obtained, and corresponding to those in fig. 2.

Krypton was the next gas investigated. Before its introduction the discharge tube was evacuated as completely as possible and rinsed first with oxygen and then with the gas itself.

The colour of the discharge was greenish, there being a considerable amount of light in the dark space. The gas first used contained sufficient argon to be visible spectroscopically, but the results were not appreciably affected when this gas was sparked with oxygen which was then removed with phosphorus, the residue condensed in liquid air, and a small heavy fraction which appeared to be very pure krypton taken.

When using krypton an unexpected difficulty was encountered. The anode, which was a plane disc parallel to the cathode, had been used previously for other experiments, and had three small holes pierced in it near the edge. When the gas was at a fairly high pressure, a small secondary discharge frequently passed through one or more of these holes, and often assumed beautiful shapes and colours. Its behaviour appeared to be quite erratic, and, as the difference of potential across the tube only fell by 5 volts when it was passing, it was considered more advisable to allow for its presence than to cut down and rebuild the whole discharge tube.

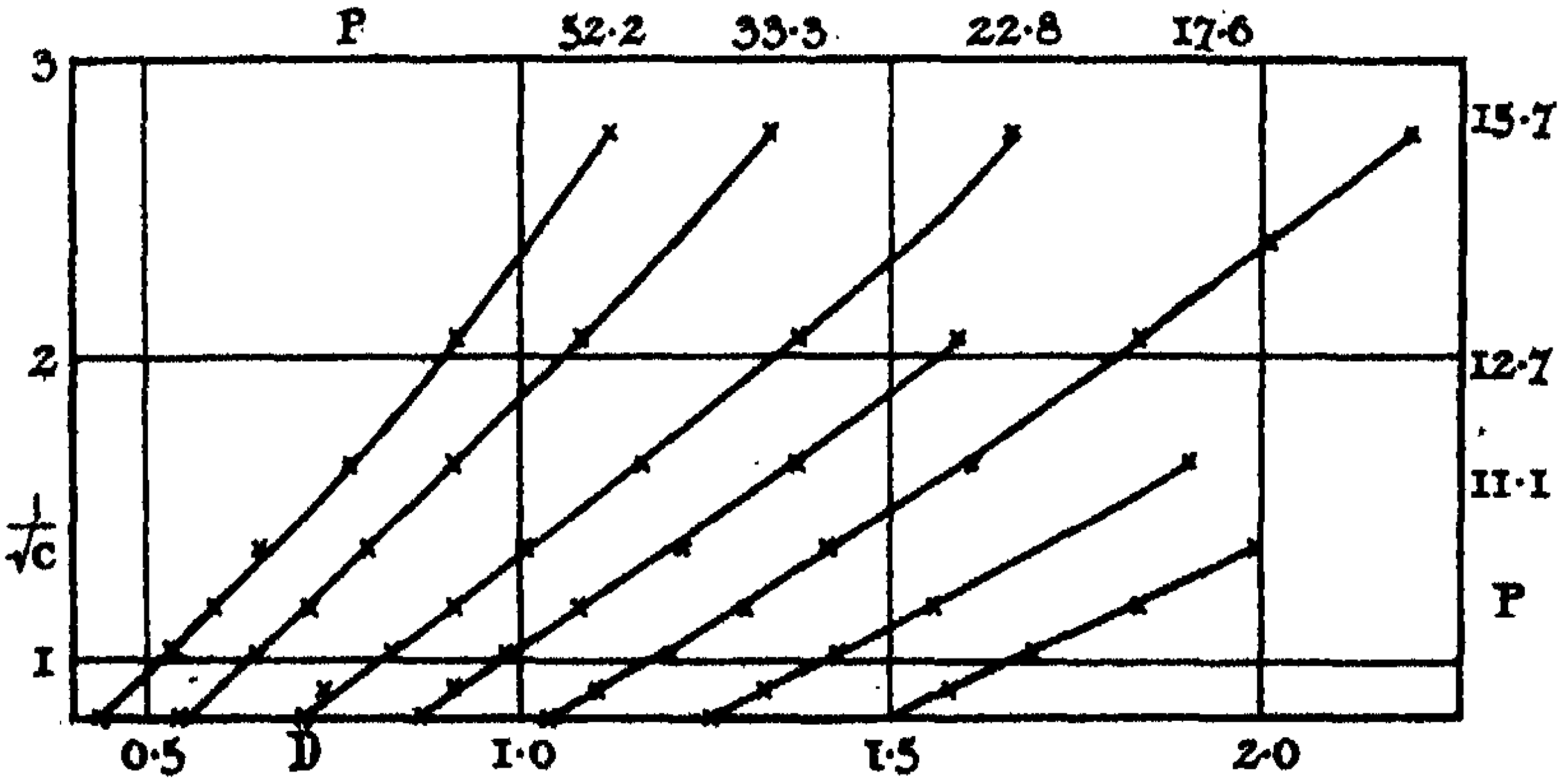

Fig. 3.—Neon—Relation between Dark Space and Current Density.

Another restriction when using krypton was the fact that if the current density exceeded about 0·10 milliampère, the discharge passed from the back of the cathode as well as from the front, as in the case of carbon monoxide. This change in the nature of the discharge appeared to be independent of the pressure.

The edge of the dark space was difficult to locate owing to small contrast, but the curves connecting the length of the dark space and the reciprocal of the square root of the current density were very similar to those for neon, that is to say, straight lines at high current densities. These lines were, however, very nearly parallel, therein differing from the neon lines.

The $V\sqrt{C}$ curves were also of the same type as those in fig. 2, but the bend was even more sudden. In fact, each curve could be well represented by two straight lines. The bend occurred at approximately the same current density as that in neon.

The case of *xenon* was similar. The gas was frozen in liquid air, and foreign gases removed by pumping, until a high vacuum was obtained. The residue appeared to be very pure xenon. The apparatus was thoroughly rinsed before the experiments were started.

The appearance of the discharge was very beautiful. Starting from the cathode, there was first a very dark and well-marked primary dark space, and then a bright olive green glow, becoming deeper green with increased distance from the cathode. This constituted the Crookes dark space. The negative glow was bluish-white, merging into orange, and the boundary of the dark space, though fairly sharp, was very difficult to measure owing to lack of contrast.

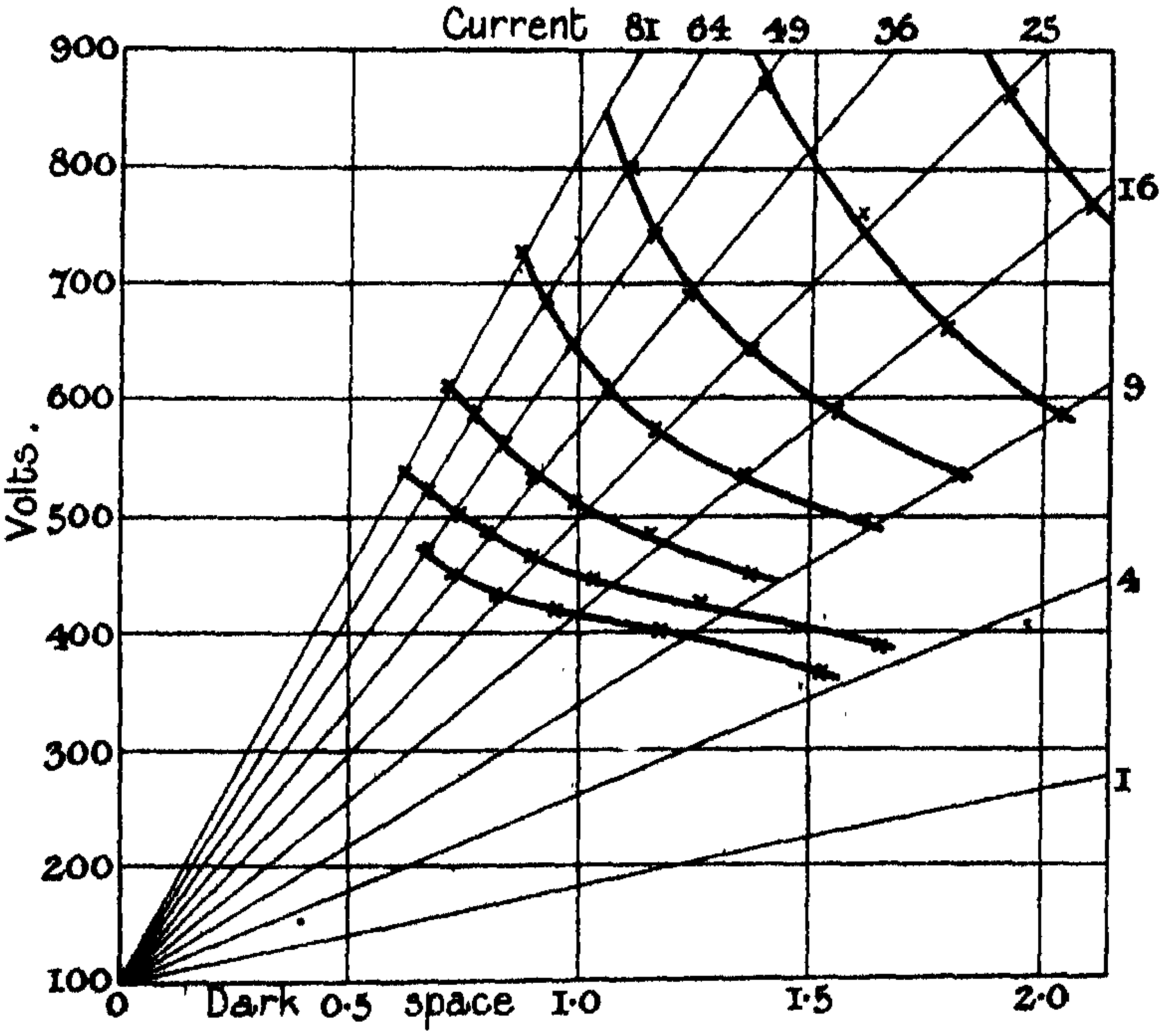

FIG. 4.—The above diagram shows the relation between the length of the dark space and the voltage in the case of krypton. The concurrent straight lines are drawn in such a way that the crosses representing the experimental results obtained would lie upon them if the relation $V-G = KD\sqrt{C}$ were rigidly true, each line being the locus of points for which the current is constant. Before drawing them, the position of the point at which they meet was determined by extrapolation. The lines crossing this pencil are the loci of points for which the pressures are equal, the actual pressures drawn being, starting from the bottom, 17·6, 14·2, 11·6, 9·2, 7·5, 6·3, and 5·2, hundredths of a millimetre.

The same phenomenon of discharge through the anode as in krypton was noted, and the current density at which the discharge started from the back of the cathode was rather less than half that in the former case, so that high current densities could not be investigated.

The forms of the curves connecting the length of the dark space, the current density, and the voltage were very similar to those in the case of krypton, but the bend in the V, $\sqrt{C}$, curves was not so marked.

The results given by *argon* were similar to those from neon. Owing to the presence of mercury vapour which could not be removed entirely by freezing a side tube connected with the apparatus in liquid air, the spectrum of the negative glow showed only mercury lines except at the boundary of the dark space where the glow was white, and argon lines showed as well. The dark space itself was red, and showed the argon spectrum with a few very faint mercury lines. At lower pressures the dark space became bluer, and argon lines appeared in the negative glow. The curves connecting the length of the dark space with the current density were of the usual type, but the V, $\sqrt{C}$, ones were much straighter than in the case of neon. There was, however, a slight bend at the same current density as in the other gases, and the curves were similar to those yielded by neon in the early experiments. It is very probable that this was due to a slight trace of oxygen, for although the argon was treated with phosphorus and subsequently distilled, it is quite likely that all the oxygen was not removed.

The phenomena occurring in *helium* were very complicated and difficult to investigate, as there appeared to be two forms of discharge. The changes were most marked when observations of the current and voltage were made at constant pressure.

Usually on taking readings after a change in pressure, values were obtained such that the relation between V and $\sqrt{C}$ was approximately linear. Before the voltages for the highest current densities could be measured, however, there was almost invariably a sudden drop in voltage, amounting often to 400 volts for the same current, and as more readings were taken the voltage would gradually decrease a little more, until what was apparently a minimum was reached. Very often before this was attained the voltage rose again. Sometimes the reverse was the case, and a series of low readings was first obtained until, without warning, the voltage would increase beyond the limits of measurement. The following account of a particularly erratic specimen of gas at a pressure of 1·5 mm. is taken from the original notes:—

A series of readings for which the relation between V and $\sqrt{C}$ was linear was obtained. When the current through the tube was 0·81 milliampère the voltage was 368. This dropped to 185, and then rose at once to 392.

The current was next increased to 1 milliampère. The voltage dropped to 200, and in about 15 seconds rose to 450, after which it fell slowly to 425, and then again fell to 200. This occurred several times. When at the low voltage, the current was cut off and restarted with the intensity of 0·36 milliampère only. The initial voltage was 240, which rose to 284. A side tube connected to the discharge tube was next immersed in liquid air, and a heavy current run. On reducing to the previous value of 0·36 milliampère the voltage was found to be 170, which rose shortly to 255. At 0·81 milliampère the voltage dropped from 350 to 200 twice.

The actual voltage changes in this example were not very great, but at low pressures they increased largely. At the same time it was increasingly difficult on lowering the pressure to obtain the low values for the voltage.

The cause of these two kinds of discharge is difficult to determine. It seems probable, however, that what may be termed the low voltage discharge is the normal one corresponding to the discharge in the other monatomic gases, while the high voltage discharge is abnormal, and its occurrence favoured by the presence of an impurity, which is probably carbon dioxide. It would appear, moreover, that this impurity acts catalytically, firstly because the current-voltage curves obtained were quite regular and definite at different pressures, although the amount of impurity cannot have been constant, and, secondly, because, as already mentioned, the discharge rapidly altered from one type to the other, whereas it can hardly be imagined that at constant current the gas should first become more pure and then grow impure again.

There is at present no actual proof that the high voltage discharge is caused by impurity at all, but it was usually possible to obtain the low voltage discharge by cooling a portion of the apparatus for some time in liquid air, while cooling in solid carbon dioxide had no effect. On removing the liquid air the voltage would usually rise, but these simple effects were largely masked by the production and possible absorption of impurity when the current was running. There was also the effect of mercury vapour to be guarded against. Unfortunately the apparatus had not been constructed so as to remove this gas completely, and it appeared that there was a small rise in the voltage when much mercury vapour was present, but the main phenomenon of changing voltage was apparently not due to its presence, for its spectral lines appeared relatively as strongly in both forms of discharge.

To the eye there was a distinct difference between the two types. The low voltage one was characterised by the edge of the dark space being very blurry and almost invisible at low current densities owing to lack of contrast.

The dark space itself was a deep emerald green, and the negative glow a slightly paler green, except at high current densities, when it became whitish. With the high voltage discharge the negative glow was almost white (possibly owing to the greater transference of energy), and the boundary very sharp. There was no obvious spectroscopic difference between the two forms.

As far as it was possible to judge, the curves connecting length of dark space, current, and voltage were similar in type to those of the other gases. The V, $\sqrt{C}$, curves were, however, when not quite irregular, fairly straight, and, moreover, all of them extrapolated very closely to the same point for zero current.

Upon the completion of these experiments, a series was performed with oxygen for comparison with results previously obtained, and the agreement was found to be good.

It will thus be seen that, apart from small individual peculiarities, the behaviour of each of the five inactive gases is very much of the same nature, provided the experiments are conducted at constant pressure. Thus, the $1/\sqrt{C}$, D, curves are almost identical, and the V, $\sqrt{C}$, curves very similar to each other. The only marked difference in making the experiments is that the range of pressures over which they can be carried out in order to obtain similar values for the length of the dark space and the voltage is widely different, varying regularly from 1·5 – 0·2 mm. in the case of helium to 0·3 – 0·06 mm. in the case of xenon.

Owing to these facts, little information is to be gained from a cursory inspection of the characteristic curves for each gas, and consequently one curve only of each type has been reproduced. Some idea of the relative behaviour of the gases may, however, be obtained by examining the approximate values for the constants in the equations

$$D = \frac{A}{P} + \frac{B}{\sqrt{C}}, \quad V = E + \frac{F\sqrt{C}}{P}, \quad V - G = KD\sqrt{C},$$

which may be deduced from these curves.

Of the above equations, the first holds good only at high current densities, and A is by no means constant. In the second equation E can be found, since the V, $\sqrt{C}$, curves extrapolate approximately to one point where $C = 0$, but F is meaningless. The third equation, however, is much more accurate, and fairly close values can be obtained both for G and K.

Table II gives the values of these quantities. The seventh and eighth columns show the pressure and voltage for unit dark space and unit current density, the units being those given on p. 169.

Table II.

	A.	B.	E.	G.	K.	P_1.	V_1.	$P_1 10^5/V_1^2$.	$P_1 10^5/V_1^2 \times$ at. wt.
Helium ...	88	? 0·27	137	25	380	52·5	412	31	124
Neon	5·0—8·0	0·41—0·82	170—220	90	445	18·6	545	6·25	125
Argon......	4·0	0·82—0·41	190	60	530	8·3	610	2·25	89
Krypton...	3·8—5·4	0·37—0·45	225—325	100	630	8·8	745	1·50	125
Xenon ...	4·0—6·0	0·23—0·40	245	120	890	5·9	1025	0·60	78
Oxygen ...	6·1	0·48	292	135	318	11·5	460	5·45	82

The expression CPD^3/V^2, which has been shown by one of us to be proportional to the velocities of the positive ions, when certain assumptions are made,* is by no means constant for the inactive gases, but a rough comparison for the different gases may be made by considering its value under certain conditions. Column 9 shows the values for unit current and unit dark space. These appear to be approximately inversely proportional to the atomic weight, as may be seen from Column 10, which gives the product of P_1/V_1^2 and the atomic weight. It seems unlikely that the agreement in the case of helium, neon, and krypton is fortuitous. It will, however, be noticed that the figures for argon and xenon differ considerably from the others. It is possible, as mentioned before, that the argon contained a trace of oxygen, which might easily vitiate the results, whilst with xenon, the values of P_1 and V_1 are only obtained by a wide extrapolation, as the maximum current which could be measured was only half the unit current adopted. Actually, the value of 0·75 for $CPD^3 10^6/V^2$ was obtained for the highest current densities used in a series of experiments, and the variation with current density and pressure was very slight, so that it is quite possible that the extrapolated figure is too low.

With regard to the other quantities given in the tables, it is somewhat remarkable that B has very similar values for all gases. K and V_1 increase regularly with rise in atomic weight of the gas, whilst P_1 decreases, but there appears to be no simple connection between any of these quantities. The values in the table are all determined graphically from the characteristic curves of the gas, and it will be seen that the sum of G and K is approximately V_1, as it should be if the third equation on p. 178 were rigidly exact.

At present, it seems useless to evolve a theoretical discussion of the general results obtained, since our knowledge of the whole mechanism of discharge is very limited, and the data so far available insufficient. Further experiments with cathodes of different shapes are, however, in progress, and it is hoped that by this means further light may be thrown on the subject and an explanation found for the results just given. In the meantime, the present paper must remain as a statement of facts.

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* 'Roy. Soc. Proc.,' A, 1907, vol. 79, p. 85; and 1911, vol. 84, p. 534.

In conclusion, we wish to express our best thanks to Sir J. J. Thomson for the great interest he has taken in this work, which was carried out in the Cavendish Laboratory, and also to Sir William Ramsay for the loan of the krypton and xenon, which alone made the research possible.

A New Method of Determining the Radiation Constant.

By G. A. SHAKESPEAR, M.A., B.Sc.

(Communicated by Prof. J. H. Poynting, F.R.S. Received November 21, 1911,—
Read January 8, 1912.)

According to Stefan's law the rate of radiation of energy from a full radiator in surroundings at a temperature of absolute zero is $\sigma\theta^4$ ergs per cm.^{2} per sec., where θ is the absolute temperature of the radiator. If the radiator be in surroundings which are themselves full radiators, but at absolute temperature θ_1, the rate of loss of energy by radiation is taken to be $\sigma(\theta^4-\theta_1^4)$.

The classical determination of the constant σ is due to Kurlbaum,[*] who used a surface bolometer with a platinum-black surface. The rise of temperature of the bolometer when exposed to the radiation from an approximately full radiator or "black body" was observed. The radiation was then cut off, and an equal rise of temperature was produced by increasing the main current in the bolometer. It was assumed that the energy received per second from the radiator in the first case was equal to the energy received per second from the increase of current in the second case. The resulting value of σ was $5{\cdot}33\times10^{-5}$ ergs per cm.^{2} per sec. per deg.^{4}, or $5{\cdot}33\times10^{-12}$ watts per cm.^{2} per deg.^{4}.

Kurlbaum gives a summary of previous measurements of σ, and there appears little doubt that his method was a great advance on those of earlier workers, and that it was carried out with such a high degree of experimental skill as to justify confidence in the result.

Later work, however, has suggested that Kurlbaum's value is too low. Fery[†] in particular, using an entirely different method, in which he employed a receiver which was more nearly a full absorber than a plane surface of platinum black, got a much higher figure ($6 \cdot 3 \times 10^{-12}$ watts per cm.^{2} per deg.^{4}), and Todd,* from experiments on the conductivity of gases, deduced a value between those of Kurlbaum and Fery, viz., $5 \cdot 48 \times 10^{-12}$ watts/cm.^{2} deg.^{4}. Still more recently Fery and Drecq† have obtained the value $6 \cdot 51 \times 10^{-12}$ watts/cm.^{2} deg.^{4}.

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[*] 'Ann. d. Phys.,' 1898, vol. 65, p. 746.

[†] 'Compt. Rend.,' April 5, 1909.

The method to be described in the present paper suggested itself to the writer in an investigation into the relative radiation and conduction losses from a heated surface at the temperature of boiling water in surroundings at ordinary room temperatures. The method is not free from objection, but in the state of uncertainty of our knowledge of the constant it appears advisable to have a determination based upon experiments differing in their nature from those previously utilised.

Principle of the Method.—It is well known that a heated body placed in air in surroundings at a lower temperature loses heat in three ways: (*a*) by conduction; (*b*) by convection; and (*c*) by radiation.

If the rate of loss of heat by a body be observed in two cases, the only difference being that the nature of the radiating surface varies, other conditions remaining the same, we shall probably be nearly correct in assuming that losses (*a*) and (*b*) will be the same, and that the difference between the observed rates of loss of energy in the two cases will be due to the difference of radiation losses only. If now these two different surfaces, at the temperature of boiling water, be exposed in turn to a radiomicrometer at the room temperature, we get the ratio of the rates of reception of energy from the two surfaces by the vane of the radiomicrometer.

Let us suppose the hot body to be a plane metal plate at 100° C. embedded in some badly conducting material, the upper surface of the plate being left free.

First let the free surface be lamp-blacked and maintained, by electrical or other means, at a temperature of 100° C. ($= \theta_1$ absolute). If we expose this surface to the radiomicrometer, the receiving surface of which consists of a lamp-blacked copper vane at a temperature of 15° C. ($= \theta_2$ absolute), we shall get a certain deflection $= D_1$.

Let $R_{B_1B_2}$ be the energy radiated per second from a square centimetre of the blackened hot-plate at temperature θ_1 when exposed to the blackened cold surface of the vane at temperature θ_2 (these conditions are indicated by the suffixes), and let $R_{B_2B_1}$ be the energy radiated per second from a square centimetre of the blackened vane at temperature θ_2 to the hot blackened plate at θ_1.

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* 'Roy. Soc. Proc.,' 1909, A, vol. 83.

† Fery and Drecq, 'Journ. de Phys.,' July, 1911, p. 558.

Then $D_1 = M(R_{B_1B_2} - R_{B_2B_1})$, where M is a constant. Now let the lamp-black be removed from the hot-plate, and let the surface of the plate be polished, raised to the temperature θ_1, and exposed, as before, to the radio-micrometer. Let the deflection be D_2. Then if $R_{P_1B_2}$ be the energy radiated per second from a square centimetre of the polished surface at θ_1 to the blackened surface at θ_2, we have

$$D_2 = M(R_{P_1B_2} - R_{B_2P_1}). \quad \text{Hence} \quad \frac{D_1}{D_2} = \frac{R_{B_1B_2} - R_{B_2B_1}}{R_{P_1B_2} - R_{B_2P_1}}.$$

Let $\frac{D_1}{D_2} = K$, hence $\frac{K-1}{K} = \frac{(R_{B_1B_2} - R_{B_2B_1}) - (R_{P_1B_2} - R_{B_2P_1})}{R_{B_1B_2} - R_{B_2B_1}}$.

Now let the hot-plate be again blackened and placed beneath, and at a short distance from, an extended parallel surface of lamp-blacked copper at temperature θ_2, the hot-plate being kept at temperature θ_1 by electrical or other means. Then if C represent the combined conduction and convection losses per second, and $L_{B_1B_2}$ the total loss of energy per second by the hot-plate in these conditions (*i.e.* the energy supplied by the electric current), we have

$$L_{B_1B_2} = C + A(R_{B_1B_2} - R_{B_2B_1})(1-b),$$

where A is the area of the radiating surface of the hot-plate and b is the reflection coefficient of the cold surface.

The factor $(1-b)$ is necessary, because the hot-plate will receive back a small fraction b of the radiation which it sends to the cold surface.

If the blackened surface be now replaced by the polished one, we have

$$L_{P_1B_2} = C + A(R_{P_1B_2} - R_{B_2P_1})(1-b) \text{ nearly.}$$

(This is not quite true, but a more detailed investigation, to be given later, shows that, in the circumstances, it is sufficiently nearly correct.)

Let $L_{B_1B_2} - L_{P_1B_2} = E$. Then

$$\begin{aligned} E &= (1-b)A\{(R_{B_1B_2} - R_{B_2B_1}) - (R_{P_1B_2} - R_{B_2P_1})\} \\ &= (1-b)A \cdot \frac{K-1}{K} \cdot (R_{B_1B_2} - R_{B_2B_1}) \\ &= (1-b)A \cdot \frac{K-1}{K} \cdot \sigma'(\theta_1^4 - \theta_2^4), \end{aligned}$$

so that

$$\sigma' = \frac{K}{K-1} \cdot \frac{E}{(1-b)A(\theta_1^4 - \theta_2^4)}.$$

We have assumed that $R_{B_1B_2} - R_{B_2B_1} = \sigma'(\theta_1^4 - \theta_2^4)$. It is necessary, therefore, to obtain σ from σ', and to do this we may expose in turn to the radiomicrometer a full radiator (*i.e.* a small hole in a constant temperature enclosure) and the lamp-blacked surface, used both at the same temperature.

Probably we may assume that the ratio of the deflections gives the ratio σ/σ'.

Experimental Details.—The quantities to be determined experimentally are thus E, K, b, and σ'/σ. Of these, all except E can be obtained from experiments with the radiomicrometer. We will consider first the determination of E.

We have to measure the rate of loss of heat from the blackened and the polished surfaces respectively when these are kept at a known temperature of about 100° C. in surroundings at about 15° C. This might be done in many ways, but the following three methods suggested themselves as likely to prove suitable: (*a*) by observing the rate of cooling of a cylindrical or spherical vessel containing a liquid at temperatures in the neighbourhood of 100° C.; (*b*) by passing steam into a spherical vessel and weighing the steam condensed in a given time; and (*c*) by keeping a surface hot by electrical means and determining the loss of energy by applying Joule's equation. Of these methods (*a*) was found not to lend itself to accurate measurement; (*b*) had many advantages, and could probably have been made to give excellent results; but (*c*), which was found to be very convenient in working, was ultimately adopted.

In applying the electrical method of heating, considerable difficulty was found in keeping the whole of any large surface at a sufficiently uniform temperature. For this reason it was considered advisable to use a comparatively small area of about 100 sq. cm. The form of apparatus ultimately adopted, which for convenience we may designate the "hot-plate," was constructed in the following manner:—

Two square plates, each of 10 cm. edge, were cut from a sheet of copper 0·3 cm. thick. These were heavily plated with silver, one side of each being polished. Two square sheets of mica, each of about 10·2 cm. edge, were also cut. The mica sheets were laid on one of the copper plates, and a row of holes was drilled through the copper and the mica along each of two opposite sides of the square, very near to the edges, the holes being equally spaced. One of the mica sheets was now removed, and short pegs of porcelain were fitted into the holes in the copper plate, forming a number of equidistant teeth, which projected about 0·1 cm. above the surface of the mica which lay on the copper plate. Bare manganin wire was wound backwards and forwards across the plate round these pegs, so as to form a sort of grid of equidistant parallel bars stretching across the plate about 0·25 cm. apart.

The other sheet of mica was now placed over the grid, the holes in the mica fitting on to the upper ends of the pegs. Over the mica the upper copper plate was laid, and was screwed tightly to the lower plate with two small screws. The whole formed a compound plate about 0·7 cm. thick, of which the outer surfaces were silvered and highly polished. The manganin wire in the middle was insulated from the copper by means of the mica. This grid constituted the electric heater.

A square flat box of copper was made, about 12 × 12 × 1·5 cm., the sides of which projected upwards above the top about 1·5 cm. all round, forming a sort of dish, in which the plate was laid on felt, so that the upper surface of the plate was parallel to and slightly below the tops of the edges of the box. The edges of the plate were also packed round with the felt up to the level of the top of the plate. The hollow box itself (forming the bottom of this dish) had an inlet and an outlet, through which water could be made to circulate. A baffle-plate was arranged inside this box to ensure that the water swept well along the upper surface of the cavity. This copper box containing the plate was fitted into a wooden frame, to which were attached two terminals, and to these terminals the ends of the wire of the heater were soldered.

The cold surface formed the lower face of another flat copper box about 15 by 15 cm., through which water

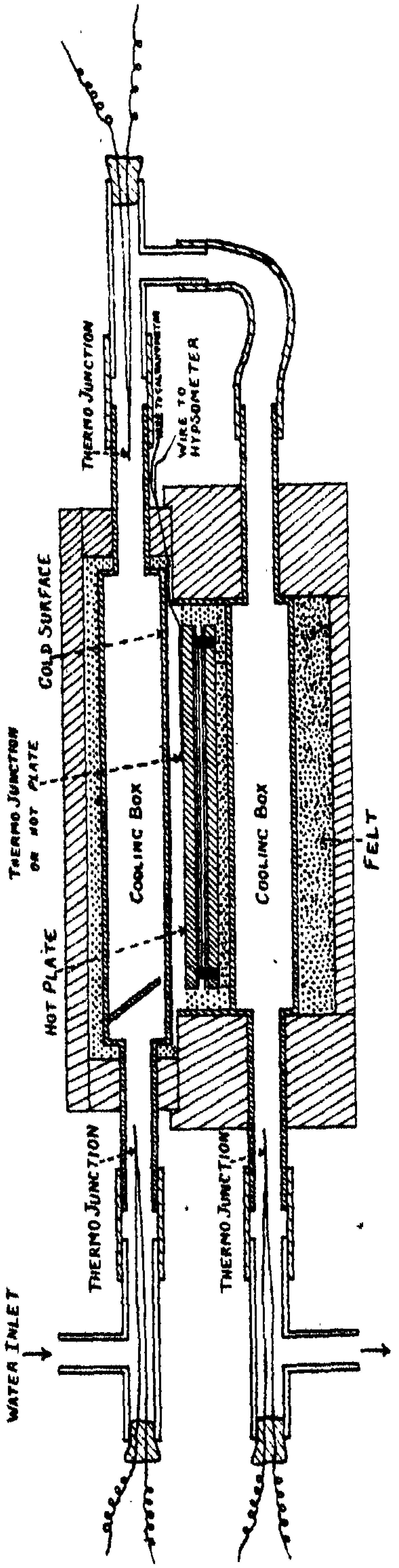

Fig. 1.

circulated before passing to the lower box. This cooling box was surrounded with felt and fitted into a wooden frame. When this frame was laid on that of the hot-plate, the hot and cold surfaces were parallel and at a distance of about 0·4 cm. apart. Fig. 1 shows the arrangement in section.

Temperature Measurements.—The temperature of the exposed surface of the hot-plate was kept at the boiling point of water by means of the electric heater. To enable this temperature to be kept accurately, a thermocouple of thin copper and constantan wires was used, one junction being kept in the steam of boiling water in a hypsometer, while the other was kept in contact with the surface of the hot-plate. At first this second junction was soldered to the plate, but it was found more convenient later to screw it down to the surface by means of a small screw. The point of contact was about half-way between the centre of the plate and the middle of one edge. The couple was used in connection with a moving-coil galvanometer, which gave about 800 scale divisions for one degree difference of temperature of the junctions. Subsidiary experiments showed that the temperature of the plate could be kept steady at the boiling point with a maximum difference of temperature between different parts of the plate of less than 0·05° C. By the application of an adjustable safety valve the temperature of the steam could be kept at 100° C. when the barometer was below 76 cm., and a sort of negatively acting safety valve in connection with a water pump enabled the temperature to be kept at 100° C. when the barometer was above 76 cm. It was found best in practice, however, to have the water boiling under atmospheric pressure and to calculate the boiling point from the height of the barometer.

It was necessary to ascertain whether, when the galvanometer indicated thermal equilibrium between the junction in the steam and that on the plate, the plate was really at the temperature of the steam. This is a very difficult problem, and I do not know of any means whereby the temperature of a hot radiating surface can be determined with certainty. A solution was sought in the following manner: A thermocouple of thin constantan and copper wires was made, the two junctions being as similar as possible. Each of these junctions was laid on the centre of the flat end of a cork, the constantan wire being bent down along one side of the cork and the copper wire along the other side, and the two wires were then bound to the cork with string. The two corks were as similar as possible.

To obtain a surface the temperature of which might be presumed to be extremely near the boiling point, a hollow copper box in the form of a cylinder about 8 cm. diameter and 3 cm. deep, was heated by passing through it a current of steam. The hot-plate was then heated electrically until the thermo-junction attached to it was in equilibrium with the junction in the hypsometer, as indicated by the above-mentioned galvanometer. The two corks, with their thermo-junctions attached, were now taken and pressed one on the steam-heated surface and the other on the hot-plate, the difference of temperature of the two junctions being observed by the deflection of a galvanometer to which they were connected. This galvanometer gave a deflection of 500 divisions of the scale for 1 degree difference of temperature of the junctions. The two junctions were then interchanged, the one which was previously on the hot-plate being now placed on the steam-heated surface, while the one from the steam-heated surface was transferred to the hot-plate. This was done to compensate for any want of symmetry between the two junctions. In this way it was found that the temperature of the hot-plate was about 0·20° C. higher than that of the steam-heated surface. Hence a correction has to be made by adding 0·20° to the temperature of the steam to obtain the temperature of the hot-plate when its thermo-junction is in equilibrium with that in the hypsometer. One would expect some such effect on account of the conduction of heat along the wires from the junction.

The temperature of the cold surface was determined by means of a thermometer placed in the outflowing stream of water. The temperature indicated by this thermometer was slightly higher than that of the water in contact with the cold plate, because the stream after leaving the cold plate had circulated under the containing box of the hot-plate, absorbing during this circulation the heat conducted through the felt from the hot-plate. Thermo-junctions placed in the stream (*a*) at the entrance to the cold plate, (*b*) at the exit from the cold plate, and (*c*) near the thermometer at the exit from the box containing the hot-plate, enabled one to calculate the difference of temperature of the stream in the middle of the cold plate and at the thermometer. It was found in this way that the mean temperature of the water in its passage over the cold plate was 0·15° lower than that of the final efflux.

The rate of flow of the water was kept as nearly as possible constant throughout the experiments.

It was next necessary to ascertain whether the mean temperature of the water passing over the cold plate accurately represented the mean temperature of the cold plate itself. In a somewhat similar case Todd* found a difference of 0·4° between the temperature of the water and that of the plate, and he found that this difference was independent of the rate of flow. In the present experiment a difference of 0·29° C. was found, the plate being 0·29° C. warmer than the water flowing over it. The difference

* 'Roy. Soc. Proc.,' 1909, A, vol. 83.

depended upon the rate of flow of the water, and for less rapid rates of flow than that employed the difference exceeded 0·5° C. (The discrepancy between this result and that of Todd can be partly accounted for, I think, by the form of his apparatus, in which the tube carrying the outflowing water passed through the inflowing stream.) The temperature of the cooling stream could be raised in cold weather by heating, with gas, a copper tube through which the water passed on its way to the cold plate. In later experiments, however, the temperature of the water in the mains rose to over 20° C., and it was found most convenient to use the water at the temperature at which it came, and if the temperature in the experiment with the black hot-plate differed from that with the polished one a correction was made, the amount of the correction having been determined from separate experiments. If this variation of temperature was considerable the experiments were rejected.

The thermometer used in measuring the temperature of the efflux water was compared with an air thermometer and found to be 0·05° C. too low in the neighbourhood of the temperatures used.

The Radiating Surfaces.—The object to be attained was the provision of a surface which could be altered with ease from one of high radiating properties to one of low.

In the calculation the fraction K/(K−1) occurs, where K is the ratio of the deflections of the radiomicrometer when the two surfaces are successively exposed to it. It is evident that if K be great compared with unity, this fraction will become sensibly equal to 1, and great accuracy in determining K is not required. Hence it was found convenient to use a highly polished surface of silver, which, when required, could be converted into a black surface by holding it in the smoke of a flame of benzene. The radiating copper plate was therefore thickly plated with silver, which was polished as highly as possible. When it was to be smoked the plate was held in position by two temporary clamps, one at each of two opposite corners. A good deal of practice was necessary to enable one to give the surface a uniform coat of soot of about the same thickness each time. The surface of the cold plate also was blackened with benzene smoke. Both the cold surface and the radiomicrometer vane were of copper, blackened in this way.

Measurement of the Energy Supplied.—The current in the heating grid was measured with a Weston ammeter of excellent construction, recently readjusted by Messrs. Elliott, and capable of being read to 0·001 ampère. The instrument was tested with a potentiometer for the range of current used and no error could be detected; it is probable therefore that the current measurements are correct to 0·001 ampère. The resistance of the grid was measured with sufficient accuracy with a resistance box made by the Cambridge Scientific Instrument Company.

Determination of K, *b, and* σ'/σ.—For the purpose of these comparisons a Boys radiomicrometer was used, the receiving vane being a plane surface of thin copper blackened with soot. This, of course, did not constitute a full absorber, and it was therefore thought advisable to check the results obtained therefrom with those yielded by a different apparatus, in which a more complete approximation to a full receiver was attained. This consisted of a single thermo-couple of Sb-Bi (each strip being about 0·3 × 0·05 × 0·01 cm.) one junction of which was soldered to a thin copper disc 0·2 cm. diameter. The disc was blackened and placed in a slightly larger hole in the centre of a brightly silvered disc of about 2 cm. diameter, which formed the diametric plane of a hemispherical cavity 2 cm. in diameter. The disc and hemisphere were of copper, silvered and highly polished. A hole 0·2 cm. in diameter, at the pole of the hemisphere, admitted radiation from the hot body to the receiving disc of the thermo-couple. Thus, any radiation falling on the black disc and diffusely reflected would be, to a large extent, reflected back to the disc. This hemisphere was mounted inside a brass tube fitted with a series

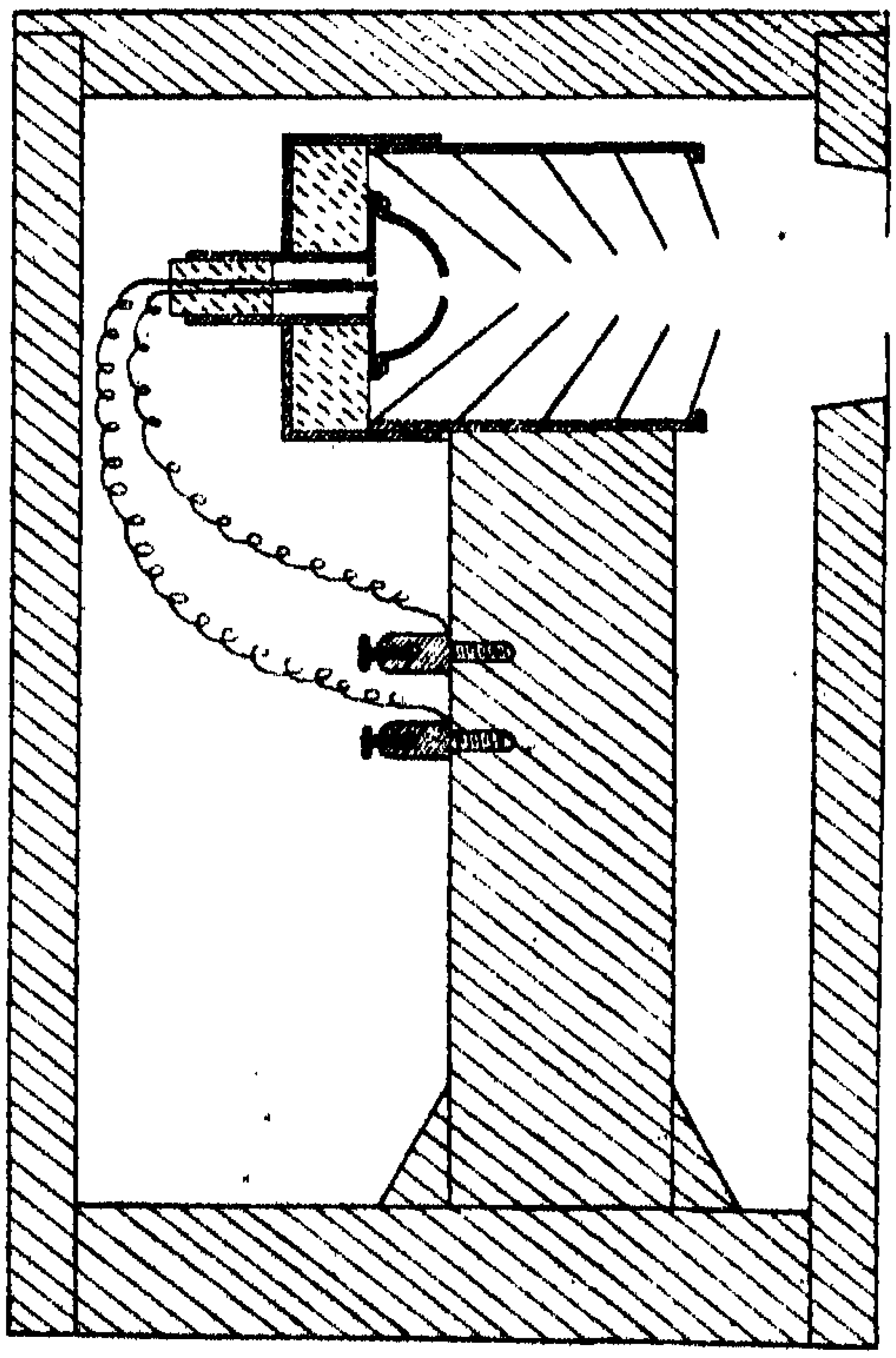

FIG. 2.

of conical diaphragms of silvered copper blackened on the side facing the hemisphere, and brightly polished on the side facing the hot body. The arrangement is shown in section in fig. 2. The whole was placed inside a protecting wooden box and used in conjunction with a low resistance Broca galvanometer. A comparison of the radiation from the hot surfaces with this instrument gave results sensibly the same as those given with the radiomicrometer; the latter, however, being much more convenient in practice, was afterwards always used for measuring the quantity K. The agreement between the two methods of comparison would seem to show that the selectiveness of the absorption exercised by the lamp-blacked copper vane of the radiomicrometer is very slight for the wave-lengths used.

A large water-cooled screen, with an aperture 2 cm. in diameter, protected the radiomicrometer from the heat of the hot-plate. The aperture could be opened or closed by means of a water-cooled shutter worked from a distance with a lever.

The ratio K was found to be usually between 51 and 57, the latter figure being given when the silver surface was most highly polished and the lamp-black coat at the most effective thickness.

Relation between the Lamp-black Surfaces and the Full Radiator.—For the purpose of finding the best thickness of soot, a steam-heated flat box of copper, one face of which could be smoked, was used. The results obtained agreed fairly well with those of Kurlbaum,[*] the maximum effect being given with a layer of about 40 mgrm./dm.^{2}. The deflection of the radiomicrometer due to the blackened surfaces was compared with that produced by the radiation from a steam-heated "black body" or full radiator. This "black body" was made in the form of a cylinder, with hollow walls, in which steam circulated. The internal diameter was 31 cm. and the length was about the same. The ends of the cylinder were closed with two hollow discs, one of which had a central circular aperture of 2·3 cm. diameter. The object of constructing the "black body" in sections was to enable it to be smoked all over the interior surface. The hollow vessel thus built up was enclosed in a double thickness of thick felt, in which an opening was left over the aperture of the cavity. The curved part and the two end pieces had each a separate inlet and outlet tube for the steam. When the "black body" was used with the radiomicrometer, diaphragms were arranged so that the receiving surface received radiation from the interior of the cavity only. In consequence of the relative smallness of the aperture as compared with the whole of the internal surface, this was probably a close approximation to the theoretical full radiator.

[*] 'Ann. d. Phys.,' 1899, vol. 67, p. 846.

An unexpected fact, namely, that *the radiation from a lamp-black surface depends upon the nature of the surface upon which the lamp-black is deposited*, was revealed in the course of these experiments in the following way:—

When the steam-heated blackened copper radiator had been given a thickness of soot which gave the maximum radiation, the silvered hot-plate was smoked and raised to the boiling point, as indicated by the thermo-junction, and then exposed to the radiomicrometer. It was not found possible to get so great an effect from this plate as from the steam-heated blackened copper surface. It was suspected that this might be due to some defect in the means of measuring the temperature of the surface of the plate, and that the plate might be below the boiling point. A flat copper box was therefore made, with steam inlet and outlet, the two opposite faces being as similar as possible. One of these flat faces was silvered and brightly polished, the other being left in the natural condition of dull unpolished copper. Both faces were then smoked, and the radiations from them at the boiling point were compared. It was found here also that the smoked silvered surface gave a less effect than the smoked copper, the former producing sensibly the same effect as the smoked silvered hot-plate. Perhaps the explanation is to be found in the inability of both lamp-black and polished silver to emit waves of certain lengths, the lamp-black being transparent to them and the silver perfectly reflecting.

The maximum effect of smoked copper at 100° C. was found to be nearly 98 per cent. of that of the full radiator, whereas the maximum effect of smoked polished silver was only about 95 per cent. Hence the reflection coefficient (b) of the blackened copper cold surface may be taken as about 0·025, and the maximum value of σ'/σ was 0·95. It may be observed that Kurlbaum* found that lamp-blacked platinum gave a maximum of about 95 per cent. of the radiation of a "black body," and he attributed this to the temperature gradient in the body of the lamp-black. In view of the present experiments, this conclusion would seem to require some revision.

Method of Carrying Out a Determination of σ.—We are now in a position to consider the course of a typical experiment for the determination of σ. The procedure was as follows: A current, larger than that which would be required ultimately, was put on to the heater, and the gas was lighted under the hypsometer, which contained one of the junctions of the thermo-couple, the other junction of which was attached to the hot-plate. In about 10 minutes the water in the hypsometer boiled, and it was generally found that the hot-plate had reached a temperature rather higher than the boiling point. The water was now turned on to the cooling boxes, and the electric current was adjusted until the spot of light on the galvanometer scale remained practically stationary at the zero point. When the current was thus properly adjusted, an increase of 0·001 ampère caused the spot of light to move slowly to the right, and a decrease of 0·001 ampère caused the spot to move slowly to the left. When the conditions were favourable, the spot could be got to remain almost motionless for hours, but usually a slight change of temperature of the cooling stream, or a rise or fall of the barometer, would necessitate small changes of the current to maintain the steady condition. When this steady state was reached, the temperature of the outflowing water was read, and the height of the barometer was observed.

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* 'Ann. d. Phys.,' 1899, vol. 67, p. 846.

The hot-plate was now exposed to the radiomicrometer, and the mean of about twenty deflections due to successive exposures of equal duration separated by equal intervals of time (20 seconds) was observed. If the plate had previously been bright the current was disconnected and the surface was smoked; the current was again turned on, the temperature of the plate was raised to the boiling point, and the plate was again exposed to the radiomicrometer as before. The cold surface was then fitted over the hot-plate, and the current was again adjusted until the steady state was reached.

The soot was then swept off the plate with a camel hair brush and weighed. The plate was again polished with a little very soft cotton wool, replaced under the cold plate, and the current once more adjusted to obtain the steady state. Immediately before or after the exposure of the plate to the radiomicrometer the " black body " was exposed to the instrument and the deflection observed.

It was found that the polished silver gave practically always the same deflection as compared with that given by the " black body," and so this part of the experiment was often omitted in the later work. As some time was required for the " black body " to reach the boiling point, it was found convenient to make the comparison of the plate with a standard lamp-black consisting of the flat steam-heated copper box above mentioned, smoked so as to give its maximum radiation. This standard itself was compared with the " black body " from time to time.

The area of the hot-plate was found by measurement with a travelling microscope.

In the latest experiments the plate was fixed in its box with a small peg of ebonite at each corner, the pegs also serving as spacing pieces to secure constancy of distance between the hot and cold surfaces. One advantage of this arrangement was that the hot plate could be used either under or over the cold plate; in the latter case there would be presumably no convection, whereas in the former some might occur. Experiments made with the hot plate first below and then above the cold plate showed that the effect of convection was extremely small, the heat loss being due almost entirely to radiation and conduction.

The following data are the results of a typical experiment:—

Resistance of heater	13·26 ohms.
Area of plate	101·7 cm.^{2}.
K	57
Reflection coefficient of cold surface = b	0·025
Deflection of radiomicrometer by blackened hot plate	46·7 divs.
Deflection by "black body."	50·0 divs.
Hence σ'/σ	0·934
Temperature of polished surface (corrected)	99·9° C.
Temperature of cold surface (corrected)	19·6° C.
Balancing current	1·13 amp.
Temperature of blackened surface (corrected)	99·9° C.
Temperature of cold surface (corrected)	19·6° C.
Balancing current	1·321 amp.
Thickness of layer of lamp-black	40 mgrm./dm.^{2}

Then

$$\sigma' = \frac{K}{K-1} \cdot \frac{E}{A\,(372{\cdot}9^4 - 292{\cdot}6^4)\,(1-b)}$$

$$= \frac{57}{56} \cdot \frac{(1{\cdot}321^2 - 1{\cdot}130^2)\,13{\cdot}26}{101{\cdot}7\,(1{\cdot}201 \times 10^{10}) \times 0{\cdot}975} = 5{\cdot}30 \times 10^{-12} \text{ watts/cm.}^2 \text{ deg.}^4,$$

so that $$\sigma = \frac{5{\cdot}30 \times 10^{-12}}{0{\cdot}934} = 5{\cdot}67 \times 10^{-12} \text{ watts/cm.}^2 \text{ deg.}^4.$$

The value of σ ultimately obtained is derived from six experiments in which the conditions were so favourable that no correction for change of temperature of the cooling stream or of the steam was necessary. The data for these experiments are given on p. 193.

Twenty experiments, which were rejected because the height of the barometer or the temperature of the cooling stream varied during the operation, gave results varying between the extreme values $5{\cdot}83 \times 10^{-12}$ and $5{\cdot}49 \times 10^{-12}$, with a mean of $5{\cdot}66 \times 10^{-12}$.

The present work may therefore be regarded as giving the value $\sigma = 5{\cdot}67 \times 10^{-12}$ watts per cm.^{2} per deg.^{4}, or $5{\cdot}67 \times 10^{-5}$ ergs per sq. cm. per sec. per deg.^{4}.

It may be of interest to observe that other experiments were made in which the polished plate was painted with aluminium paint, the two radiating surfaces being in this case the aluminium paint and the lamp-black. The value of K was very variable, but when the paint had been

Temp. of hot-plate (corr.).	Temp. of cold surface (corr.).	Balancing current.	Ratio σ'/σ.	Thickness of lamp-black.	σ'.	σ.
° C.	° C.	ampères.		mgrm./dm.^{2}	watts/cm.^{2} deg.^{4}	watts/cm.^{2} deg.^{4}
99·79	15·80	Black...... 1·310 Bright ... 1·115	0·920	74	$5·21 \times 10^{-12}$	$5·66 \times 10^{-12}$
99·94	16·00	Black...... 1·318 Bright ... 1·114	0·960	56	$5·46 \times 10^{-12}$	$5·67 \times 10^{-12}$
99·90	19·60	Black...... 1·321 Bright ... 1·130	0·934	40	$5·30 \times 10^{-12}$	$5·68 \times 10^{-12}$
100·24	20·20	Black...... 1·319 Bright ... 1·129	0·934	40	$5·28 \times 10^{-12}$	$5·65 \times 10^{-12}$
99·90	20·00	Black...... 1·313 Bright ... 1·122	0·936	44	$5·29 \times 10^{-12}$	$5·65 \times 10^{-12}$
99·90	19·45	Black...... 1·316 Bright ... 1·123	0·950	43	$5·38 \times 10^{-12}$	$5·66 \times 10^{-12}$
				Mean value of σ........		$5·67 \times 10^{-12}$

carefully washed it was about 4·3. Evidently an error in K is here much more serious than in the case previously described. Moreover, the difference E was much less, and the possible error had a much greater relative value. Consequently the value of σ deduced from these experiments varies widely, *e.g.*, three experiments in favourable conditions gave 5·47, 5·27, and $6·25 \times 10^{-12}$, the mean being $5·66 \times 10^{-12}$. Though no importance is attached to these experiments they may be regarded as a rough check upon the foregoing.

It may be observed that the value $5·67 \times 10^{-12}$ is much nearer to the values given by Kurlbaum ($5·33 \times 10^{-12}$) and Todd ($5·48 \times 10^{-12}$) than to that of Fery and Drecq ($6·51 \times 10^{-12}$). At the same time it should be remarked that Kurlbaum and Todd used the same range of temperature as that employed in the present work, whereas Fery dealt with much higher temperatures. On the other hand, other workers using methods similar to that of Kurlbaum have obtained values not very different from Kurlbaum's over greater ranges of temperature.* In the work of Fery and Drecq, however, if one may judge from the diagram representing the arrangement of their apparatus, there seems to be reason to expect a serious error in consequence of reflection of radiation from the inside of the aperture in the cork screen. No mention is made of any precaution to avoid such possible error, which, it may be noted, would result in too high a value for σ.

The following (for which I am largely indebted to my colleague, Dr. Guy Barlow) is a more detailed investigation of the theory of the experiment.

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* *Cf.* Valentiner, 'Ann. d. Phys.,' 1910, vol. 31, p. 275.

Let X and Y (fig. 3) represent the polished hot-plate and the blackened cold surface respectively, their reflection coefficients being p and b.

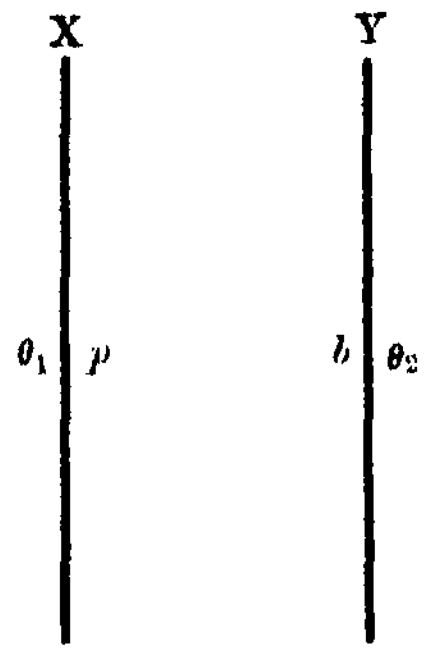

Fig 3.

Let a quantity of energy, Q, be radiated from X to Y. Of this quantity a fraction bQ will be reflected and $(1-b)$Q will be retained by Y. Of the reflected portion, pbQ will be again reflected and $(1-p)b$Q retained by X, and so on.

In the limit, X will thus receive back $(1-p)\,bQ/(1-bp)$ and Y will retain $Q\,(1-b)/(1-bp)$.

(It must be noted here that we are assuming that the coefficients b and p remain constant, which is probably not true. To make the investigation full we should require to know the value of each of these coefficients for each part of the spectrum of the radiation used. This being at present out of the question, we must make use of the approximation here adopted.)

Again, if a quantity of energy Q′ be radiated from Y an amount $Q'(1-p)/(1-bp)$ will be absorbed by X, the factor $(1-p)/(1-bp)$ being the effective absorption coefficient of X.

Now, let us assume that each square centimetre of plate X at temperature θ_1 radiates $R_1\,(1-p)$, where R_1 = full radiation $= \sigma\theta_1^4$.

Then, as we have just seen, X will receive back altogether $\dfrac{b(1-p)}{1-bp}R_1(1-p)$. And if we assume that each square centimetre of Y radiates $R_2\,(1-b)$, where R_2 = full radiation for temperature θ_2, we shall have X receiving in addition $R_2\,(1-b)\,.\,(1-p)/(1-bp)$.

If, then, the temperature of X be kept at θ_1 by electrical means, and if C represent the rate of loss of energy by conduction and convection, the rate of supply of energy by the current must be

$$R_1\,(1-p)-R_1\,(1-p)\frac{b\,(1-p)}{1-bp}-R_2\,(1-b)\,\frac{1-p}{1-bp}+C.$$

Hence, in the notation previously used, if X be the polished hot plate, we have

$$L_{P,B_2} = A\left[R_1(1-p)\left\{1-\frac{b(1-p)}{1-bp}\right\}-R_2(1-b)\frac{1-p}{1-bp}\right]+C$$

$$= A\left[\frac{(1-p)(1-b)}{1-bp}(R_1-R_2)\right]+C.$$

Similarly, if X be the blackened silver hot-plate, with reflection coefficient b', also at θ_1, we have

$$L_{B_1B_2} = A\left[\frac{(1-b')(1-b)}{1-bb'}(R_1-R_2)\right]+C;$$

so that $$E = A(1-b)(R_1-R_2)\left[\frac{1-b'}{1-bb'}-\frac{1-b}{1-bp}\right].$$

Now b is about 0·02 and b' about 0·05, while p is about 0·98. Hence we may neglect bb', so that

$$E = A(1-b)(R_1-R_2)\left(1-b'-\frac{1-p}{1-bp}\right)$$

$$= A(R_1-R_2)\left(\frac{p-b'-2bp}{1-bp}\right)$$

$$= A\sigma(\theta_1^4-\theta_2^4)\left(\frac{p-b'-2bp}{1-bp}\right).$$

The quantities p, b, and b' are given by the radiomicrometer experiments, which we may now consider.

Theory of Radiomicrometer Experiments.—We assume that the deflection of the instrument is proportional to the difference between the energy entering the radiomicrometer and that leaving it by radiation.

We also assume that the hot-plate at θ_1, when exposed to the radiomicrometer, is receiving from its surroundings full radiation at temperature θ_2.

This is probably nearly true, since the field of view, so to speak, of the hot-plate is nearly filled by the blackened surface of the large water-cooled screen in which is the small aperture admitting radiation to the radiomicrometer.

Let us now consider the quantities of energy Q_1, Q_2, Q_3, Q_4, and Q_5 respectively entering the instrument when we expose to it

(*a*) the polished silver hot-plate at θ_1,
(*b*) the blackened silver hot-plate at θ_1,
(*c*) the blackened copper surface at θ_1,
(*d*) the "black body" at θ_1,
(*e*) the "black body" at θ_2.

We have:—

(*a*) $$Q_1 = M\{(1-p)R_1+pR_2\},$$

(*b*) $$Q_2 = M\{(1-b')R_1+b'R_2\},$$

(*c*) $$Q_3 = M\{(1-b)R_1+bR_2\},$$

(*d*) $$Q_4 = MR_1,$$

(*e*) $$Q_5 = MR_2,$$

where M is a constant.

Now (*e*) gives zero deflection, therefore we may regard the energy emerging from the radiomicrometer as equal to that entering, $= MR_2$.

Hence if the deflections be respectively D_1, D_2, etc., we have

$$D_1 \propto Q_1-Q_5 = G\{(1-p)R_1-(1-p)R_2\} = G(1-p)(R_1-R_2),$$

where G is a constant.

$$D_2 \propto Q_2-Q_5 = G(1-b')(R_1-R_2),$$
$$D_3 \propto Q_3-Q_5 = G(1-b)(R_1-R_2),$$
$$D_4 \propto Q_4-Q_5 = G(R_1-R_2).$$

Thus $$\frac{D_1}{D_4} = (1-p) \quad\text{and}\quad p = 1-\frac{D_1}{D_4},$$
$$\frac{D_2}{D_4} = (1-b') \quad\text{and}\quad b' = 1-\frac{D_2}{D_4},$$
$$\frac{D_3}{D_4} = (1-b) \quad\text{and}\quad b = 1-\frac{D_3}{D_4}.$$

The result obtained from the approximate theory given earlier is equivalent to

$$\sigma = \frac{E}{A(\theta_1^4-\theta_2^4)(p-b')(1-b)}$$
$$= \frac{E}{A(\theta_1^4-\theta_2^4)(p-b'-bp)},$$

whereas that here arrived at is

$$\sigma = \frac{E(1-bp)}{A(\theta_1^4-\theta_2^4)(p-b'-2bp)}.$$

In consequence of the magnitudes of *p*, *b*, and *b'*, the two expressions are nearly identical, and the adoption of the formula given by the more detailed investigation would merely change the result from $5{\cdot}67\times10^{-12}$ to $5{\cdot}68\times10^{-12}$.

No mention has been made of any edge effect, because the "field of view" of every part of the hot radiating surface is practically filled with black surfaces at temperature θ_2.

Since the above was ready for publication my attention has been drawn to a paper by Bottomley and King,* of which I was not previously aware. The method used by these experimenters bears some resemblance to that described in the present paper, but the treatment and results differ widely.

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* 'Phil. Trans.,' 1908, vol. 208.

Determination of the Coefficient of Inter-Diffusion of Gases and the Velocity of Ions under an Electric Force, in Terms of Mean Free Paths.

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1. The properties of gases which depend on the velocity of agitation of molecules and the lengths of their free paths may easily be expressed in terms of the mean velocity of agitation and the mean free path when certain assumptions are made in order to simplify the investigations. The expressions thus found on the principles of the kinetic theory are in good agreement with the experimental results in most cases, but the formulæ that have been obtained for the coefficient of inter-diffusion of gases and the velocity of particles acted on by an external force are not so satisfactory.

The equations of motion of two inter-diffusing gases have been given by Maxwell, and it may be shown from these that the exact value of the ratio of the coefficient of diffusion of ions to the velocity under unit electric force is Ne/Π, where N is the number of molecules per cubic centimetre of a gas at pressure Π, and e the charge on an ion. The method adopted by Maxwell is perfectly general, there are no assumptions made as to the distribution of the velocities of agitation, and no particular definition of a collision or a free path is involved, so that there can be little doubt as to the accuracy of the result.

When, however, the coefficient of diffusion in terms of the mean free path and velocity of agitation that is usually given is compared with the velocity under an electric force expressed in terms of the same quantities the ratio obtained is about one-half the above value.

It is interesting, therefore, to examine these formulæ and to see how the error arises, for when the correct expressions for the rate of diffusion and the velocity under an electric force are found, it is easy to see that Maxwell's equations follow immediately from them. These investigations have been made on the supposition that the molecules travel with a constant velocity of agitation, which is the same as the mean value of that velocity.

The investigations are much simplified when this assumption is made, and no serious error is introduced, since the velocity of a molecule seldom differs by much from the mean value as is shown by Maxwell's law of distribution of the velocities, from which it may be seen that the ratio of the mean velocity to the square root of the mean square of the velocity is 12/13. A somewhat larger error would be introduced if calculations were made on the supposition that the free paths were all equal to the mean free path. It is unnecessary, however, to introduce this simplification, as it is easy to take into consideration variations in the lengths of the free paths.

For if l is the mean length of a large number N of free paths of a molecule or the mean distance that a large number of particles will travel before they collide; then the number of paths n that exceed a distance x is $n = \mathrm{N}e^{-x/l}$. The mean square of the paths is

$$\int_0^\infty x^2 e^{-x/l}\frac{dx}{l} = 2l^2,$$

or twice the square of the mean free path.

This result is frequently neglected, and in many text books it is stated that the values of the coefficients, such as that of viscosity $\eta = \frac{1}{3}mnl\mathrm{V}$, can be obtained on the supposition that the free paths are all equal to the mean free path. It is obvious that the coefficient of viscosity would be $\frac{1}{6}mnl\mathrm{V}$ if all the molecules traversed paths of length l with a velocity V.

As regards the coefficient of inter-diffusion of two gases considerable difference of opinion has been expressed as to the correct value of this coefficient. The expression usually given is $\frac{1}{3}(\mathrm{N}_1\mathrm{L}_2\mathrm{V}_2+\mathrm{N}_2\mathrm{L}_1\mathrm{V}_1)/\mathrm{N}$, N_1 and N_2 being the numbers of molecules per cubic centimetre of the two gases, L_1 and L_2 the mean free paths of the molecules, V_1 and V_2 their velocities of agitation. The numerical factor $\pi/8$ is sometimes given instead of $\frac{1}{3}$. The objection to this formula is that it gives different values for the diffusion when the proportion of the two gases $\mathrm{N}_1/\mathrm{N}_2$ is altered, which is contrary both to experimental evidence and also to the result of the simpler investigation by which Maxwell found the equations of motion of two inter-diffusing gases.

This difficulty has been avoided by Maxwell by assuming that the encounters between molecules of the same kind have no influence on the velocity of the current with which each of the two gases flow against each other, since there is no loss of momentum of a gas in any direction when two of its molecules collide. Maxwell therefore considered that the correct values to be substituted for L_1 and L_2 in the above formula are the lengths of the free paths of a molecule of one gas among the molecules of the other, so that L_1 and L_2 would be inversely proportional to N_2 and N_1 respectively, and the above expression would be independent of the ratio $\mathrm{N}_1/\mathrm{N}_2$.

The problem at present under consideration deals more particularly with the case in which a very small quantity of one of the gases is present, so that case will be investigated first, by an indirect method which is probably less complicated than that generally used.

2. The determination of the velocity under an electric force and the rate of diffusion of ions into a gas may be investigated by making the ordinary assumptions as to the nature of a collision. It will be seen that the absolute values of the coefficients may be inaccurate, but this does not affect their ratio. For the present, therefore, it will be assumed that the ions travel with a constant velocity of agitation V along free paths of various lengths of mean value l, and that after a collision all directions of motion are equally probable. Also the velocity of the ion due to the electric force is supposed to be small compared with V.

Under these conditions the velocity under an electric force may easily be found. Let m be the mass of an ion, e its charge, then under a force X it travels a distance $s_1 = \frac{1}{2}ft_1^2$ in the time t_1 between the collisions, where $f = \mathrm{X}e/m$. Substituting for t_1 its value l_1/V, then the distance S travelled in the direction X after a number of free paths of lengths $l_1, l_2 \ldots l_n$ have been traversed is

$$\mathrm{S} = \tfrac{1}{2}\frac{f}{\mathrm{V}^2}\cdot(l_1^2+l_2^2+\ldots+l_n^2) = \frac{nfl^2}{\mathrm{V}^2},$$

where l is the mean free path.

The velocity U in the direction of the force becomes $\mathrm{S}/(t_1+t_2+\ldots+t_n)$.

Hence $$\mathrm{U} = \frac{nfl^2}{\mathrm{V}^2(t_1+t_2+\ldots+t_n)} = \frac{fl}{\mathrm{V}} = \frac{\mathrm{X}e}{m}\cdot t,\text{*}$$

where $t = l/\mathrm{V}$ is the average time between two collisions.

[The expression given by Drude† and Thomson,‡ $\frac{1}{2}\frac{\mathrm{X}e}{m}t$, is one-half the correct value obtained under these conditions.]

3. The rate of diffusion of the ions into the gas may be found under similar conditions. It will be supposed that the number of ions is small compared with the number of molecules, and it will therefore be unnecessary to consider the effects of collisions between two ions. A method of investigation which is applicable to this case, and also to the more complicated case in which the effects of collisions are less precisely defined, consists in finding the rate at which the mean square R^2 of the distances of the ions from any point O increases with the time.

When the density of a distribution of ions varies with the distance x from a fixed plane, the number that cross any plane $x =$ const. per second depends on the rate of variation dn/dx of the number n of ions per cubic centimetre. Hence the mean velocity u of the ions is given by an equation of the form

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* This formula is also given by P. Langevin, 'Ann. de Chim. et Phys.,' 1903, vol. 28, p. 317.

† P. Drude, 'Annalen der Physik,' 1900, vol. 1, p. 566.

‡ J. J. Thomson, 'Conduction of Electricity through Gases,' second edition, p. 74.

$$nu = -\mathrm{K}\frac{dn}{dx},$$

where K is the coefficient of diffusion. The gas in which the ions move may be supposed to be at rest since the number of molecules of the gas in any volume is much greater than the number of ions. If this equation be adopted as giving a definition of the rate of diffusion, it is easy to find the value of $d(\mathrm{R}^2)/dt$ in terms of K for any distribution.

If a series of spheres be drawn with O as centre, then the motion with respect to the centre of the ions in the space between two spheres of radii r and $r+dr$ will be the same as if the ions are distributed uniformly in the space between the two spheres. Hence, in dealing with the motion from or towards the centre, the distribution may be considered to be symmetrical with respect to the centre, and the number n per cubic centimetre may be considered as a function of r only.

The value of R^2 is given by the equation

$$\int_0^{r'} 4\pi r^4 n\, dr = \mathrm{R}^2 \int_0^{r'} 4\pi r^2 n\, dr,$$

where the sphere of radius r' extends beyond the region throughout which the ions are distributed so that $n = 0$ and $dn/dr = 0$ when $r = r'$. The integral on the right is constant with respect to the time, being the total number of ions under consideration, so that $d(\mathrm{R}^2)/dt$ is given by the equation

$$\int_0^{r'} r^4 \frac{dn}{dt}\, dr = \frac{d(\mathrm{R}^2)}{dt}\int_0^{r'} r^2 n\, dr.$$

Also the rate at which the number of ions between the spheres r and $r+dr$ is changing is equal to the difference between the rates at which ions are crossing the two boundaries.

Hence $$r^2\frac{dn}{dt}\,dr = -\frac{d}{dr}(r^2 nu)\,dr = \mathrm{K}\,\frac{d}{dr}\left(r^2\frac{dn}{dr}\right)dr.$$

Hence $$\mathrm{K}\int_0^{r'} r^2\frac{d}{dr}\left(r^2\frac{dn}{dr}\right)dr = \frac{d(\mathrm{R}^2)}{dt}\int_0^{r'} r^2 n\, dr.$$

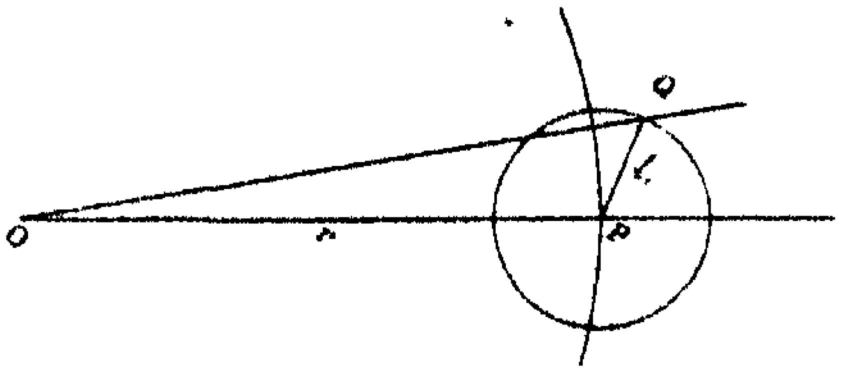
Integrating by parts, the first integral becomes

$$2\mathrm{K}\int_0^{r'} r^3\frac{dn}{dr}\,dr = 6\mathrm{K}\int_0^{r'} r^2 n\, dr.$$

Hence $$\frac{d(\mathrm{R}^2)}{dt} = 6\mathrm{K}.$$

Hence the rate of variation of the mean square of the distance of any distribution from any point is constant and equal to 6K.

4. The rate of change of the mean square of the distance of any distribution from any point O may also be investigated by considering the actual motion of the particles along their free paths.



Let a number of ions start from a point P, in all directions, with velocity V, so that after a time t_1 they will be distributed uniformly over a sphere of radius $l_1 = Vt_1$.

The mean square of their distances from O is

$$\frac{1}{4\pi l_1^2}\int_0^\pi \mathrm{OQ}^2 \times 2\pi l_1^2 \sin\theta\, d\theta = \tfrac{1}{2}\int_0^\pi (r^2+l_1^2+2rl_1\cos\theta)\sin\theta\, d\theta = r^2+l_1^2,$$

so that in the time t_1 the mean square of their distances is increased by l_1^2. If the ions collide with molecules after travelling the distance l_1 then all directions of motion become again equally probable, and along the next free path of length l_2 the mean square of the distance increases by l_2^2.

Hence $$\frac{d\mathrm{R}^2}{dt} = \frac{l_1^2+l_2^2+\dots}{t_1+t_2+\dots} = \frac{2l^2\mathrm{V}}{l} = 2l\mathrm{V} = 6\mathrm{K},$$

where l is the mean free path.

Hence $\mathrm{K} = \frac{1}{3}l\mathrm{V}$.

The ratio of the velocity under unit electric force to the rate of diffusion thus becomes

$$\frac{\mathrm{U}}{\mathrm{K}} = \frac{\mathrm{X}e}{m}\frac{l}{\mathrm{V}}\frac{3}{l\mathrm{V}} = \frac{3\mathrm{N}e}{m\mathrm{NV}^2} = \frac{\mathrm{N}e}{\Pi},$$

since $\mathrm{X} = 1$, and $\Pi = \frac{1}{3}m\mathrm{NV}^2$.

Thus the correct ratio of U/K is obtained when it is supposed that all directions of motion become equally probable after a collision.

5. The question arises whether this definition of a collision is too simple when dealing with an ion moving through a gas. The determinations of the rate of diffusion show that the ions diffuse much more slowly than molecules of gases. Thus ions generated in air diffuse much more slowly than carbonic acid through air, so that presumably the ions have masses associated with them that are large compared with the mass of a molecule. This mass may consist of a group of molecules of the gas attracted by the charge on the ion.

It is necessary therefore to consider whether the above investigation can apply when the masses of the particles diffusing into the gas under consideration are much larger than molecules of the gas.

It is difficult to state exactly how a collision should be specified, but it is obvious that if all directions of motion of a small molecule are equally probable after a collision with a large molecule, the same does not hold for the larger molecule. The particle of large mass will, in general, only be slightly deflected from its original path by an impact with a small mass which may completely reverse the direction of motion of the latter. For the masses m and m' travel with velocities V and V′, connected by the equation $mV^2 = m'V'^2$, so that the ratio of their momenta is $\sqrt{m}/\sqrt{m'}$. Hence, a transfer of momentum equal to $2m'V'$ from the larger mass m to the smaller would reverse the direction of motion of the smaller mass, and would have a comparatively small effect on the momentum mV of the larger mass. If, therefore, there be two sets of molecules, one of which are much larger than the others, and those encounters between molecules are taken into consideration which are such that all subsequent directions of motion of the smaller mass become equally probable, then, when dealing with the motion of the larger masses, it will be necessary to consider that all subsequent directions of motion become equally probable only after several collisions, each collision making a small change in the direction of motion.

In order to calculate the rate of diffusion of the ions or particles of large mass into the gas, the particles, as before, may be considered to move along rectilinear paths of lengths l_1, l_2, etc., with constant velocity V. Let u_1, v_1, w_1 be the components of the velocity along three directions at right angles, during the time t_1 while the particle traverses the first path, u_2, v_2, w_2 the components along the second path, etc. The distances x, y, z which the particle will travel along the axes in the time $t = t_1+t_2+\ldots+t_n$ will be

$$x = u_1t_1+u_2t_2+\ldots+u_nt_n,$$
$$y = v_1t_1+v_2t_2+\ldots+v_nt_n,$$
$$z = w_1t_1+w_2t_2+\ldots+w_nt_n,$$

and the square of the distance from the origin of co-ordinates becomes

$$\begin{aligned} R^2 &= (u_1^2+v_1^2+w_1^2)\,t_1^2+\ldots+2t_1t_2(u_1u_2+v_1v_2+w_1w_2)+\ldots \\ &= l_1^2+l_2^2+\ldots+l_n^2+2l_1l_2\cos\phi_{12}+2l_1l_3\cos\phi_{13}+\ldots, \end{aligned}$$

where ϕ_{12} is the angle between the first and second path, etc.

The sum of the squares of the free paths being $2nl^2 = 2l\,(l_1+l_2+\ldots+l_n)$, the expression for R^2 may be written as the sum of n terms, of which the first two are

$$2l_1(l+l_2\cos\phi_{12}+l_3\cos\phi_{13}+l_4\cos\phi_{14}+\ldots),$$

$$2l_2(l+l_3\cos\phi_{23}+l_4\cos\phi_{24}+\ldots).$$

The terms $l_2\cos\phi_{12}+l_3\cos\phi_{13}+\ldots$ are the projections of the second, third, and subsequent paths on the direction of the first path, and their sum has a value λ different from zero, since the angles between the first path and those that immediately follow are small. After a certain number of collisions, having an average value s, the angle ϕ_{1s} becomes equal to $\pi/2$. The average value of the projection of the subsequent paths l_{s+1}, etc., on the first path then becomes zero, since all directions of motion have become equally probable. The n terms in the expression for R^2 then become

$$2l_1(l+\lambda)+2l_2(l+\lambda)+\ldots,$$

where λ is the average distance the ion travels, after a collision, in the direction in which it was moving before the collision. When the number s is small compared with the total number of collisions n under consideration,

$$R^2 = 2(l+\lambda)(l_1+l_2+\ldots+l_n) = 2nl(l+\lambda).$$

Hence $$\frac{dR^2}{dt} = \frac{2nl(l+\lambda)}{t_1+t_2+\ldots+t_n} = 2(l+\lambda)V = 6K.$$

Hence $$K = \tfrac{1}{3}(l+\lambda)V.$$

6. In order to find the velocity U, due to an electric force X, under these conditions, it is to be noticed that, when an ion has velocities u, v, w along the axes before a collision, then, after colliding, it drifts on through distances distances $u\lambda/V$, $v\lambda/V$, and $w\lambda/V$, measured along the axes before all directions of motion become equally probable.

When an electric force acts during a time t_1 while an ion is traversing the path l_1 with a velocity V the distance travelled along the axis of x due to the force X is $\frac{1}{2}ft_1^2$, and, on colliding at the end of the path, the ion has a velocity ft_1 in the direction of the force. The distance the ion travels after the collision due to this velocity is $ft_1\lambda/V$. Hence the total distance S travelled in a time $t_1+t_2+\ldots+t_n$ due to the action of the force, is

$$S = \tfrac{1}{2}ft_1^2+\tfrac{1}{2}ft_2^2+\ldots+\frac{ft_1\lambda}{V}+\frac{ft_2\lambda}{V}+\ldots$$

$$= \frac{f}{V^2}\left\{\tfrac{1}{2}(l_1^2+l_2^2+\ldots)+\lambda(l_1+l_2+\ldots)\right\}$$

$$= \frac{f}{V^2}nl(l+\lambda),$$

so that the velocity U under the electric force becomes

$$\mathrm{U} = \frac{\mathrm{S}}{t_1+t_2+\ldots+t_n} = \frac{f}{\mathrm{V}}\frac{nl(l+\lambda)}{l_1+l_2+\ldots+l_n} = \frac{f(l+\lambda)}{\mathrm{V}} = \frac{\mathrm{X}e}{m}\frac{l+\lambda}{\mathrm{V}}.$$

The ratio of the velocity to the rate of diffusion $\frac{1}{3}(l+\lambda)\mathrm{V}$ is the same as before,

$$\frac{\mathrm{U}}{\mathrm{K}} = \frac{3\mathrm{X}e}{m\mathrm{V}^2} = \frac{\mathrm{N}e\mathrm{X}}{\Pi}.$$

7. It is thus seen that the ratio of the velocity under an electric force to the rate of diffusion is independent of the precise definition of the collisions. The question that remains to be decided is the value that must be attributed to l, since l is indefinite when the nature of the collisions remains unspecified, whereas $l+\lambda$ is a perfectly definite quantity, and represents the mean distance that a large number of the particles or ions will travel along an axis if they all start in that direction with a velocity V, when sufficient time is allowed for the motion of agitation to become equally distributed in all directions.

The simplest method of proceeding is to consider the case where two gases A and B are diffusing into each other, n and n' being the number of molecules of the two gases per cubic centimetre. It is obvious that, when n and n' are of the same order of magnitude, the molecules of A collide with each other with a frequency that is of the same order as the frequency of collisions between the molecules of A and B. But, as far as the relative motion of the two gases is concerned, the collisions between the molecules of the same kind can have no effect on the mean velocity of either gas. It may also be seen that such a collision has no effect on the mean square of their distances from a given point, or on the velocity under an electric force. It will be necessary, however, in this case to consider the *mean velocities* u and u' of both gases, so that if K be the rate of diffusion of A, and K′ that of B, then, by definition,

$$\mathrm{K}\frac{dn}{dx} = -n(u-u'), \quad \mathrm{K}'\frac{dn'}{dx} = n'(u-u'),$$

where K is the rate of diffusion of a small number of molecules of A, as estimated above, that is $\mathrm{K} = \frac{1}{3}(l+\lambda)\mathrm{V}$, l being the mean free path of a molecule of A in the gas B, when the latter contains n' molecules per cubic centimetre, both l and λ are inversely proportional to n'.

Since $nu+n'u' = 0$, $n'(u-u') = (n+n')u$, so that the above equations become

$$\frac{\mathrm{K}n'}{n+n'}\frac{dn}{dx} = -nu \quad \text{and} \quad \frac{\mathrm{K}'n}{n+n'}\frac{dn'}{dx} = -n'u' \quad \text{or} \quad \mathrm{D}\frac{dn}{dx} = -nu.$$

Also, since $n+n'$ is a constant at each point,

$$\frac{dn}{dx} = -\frac{dn'}{dx}.$$

Hence $$Kn' = K'n.$$

The rate of diffusion of a small number of molecules of A into B when the latter contains $n+n'$ molecules per cubic centimetre is $\frac{Kn'}{n+n'}$, since $K = \frac{1}{3}(l+\lambda)V$ and $\frac{n'}{n+n'}(l+\lambda)$ is the value of $(l+\lambda)$ when the number of molecules per cubic centimetre of B is increased from n' to $n+n'$. Hence the rate of diffusion $\frac{Kn'}{n+n'}$, (or D) is independent of the relative values of n and n', and is inversely proportional to the total pressure of the two gases.

Also, since $Kn'/(n+n') = K'n/(n+n')$, the rate of diffusion of a small number of molecules of A into a gas B, containing a large number $n+n'$ of molecules per cubic centimetre is the same as the rate of diffusion of a small number of molecules of B into the gas A, containing the same number $n+n'$ of molecules per cubic centimetre.

8. In order to find the relative values of the quantities l and λ, as used in sections 5 and 6, it is necessary to define the collisions in some way, for if every trifling deflection of the ion is taken as terminating a free path, then λ will be very large compared with l. The case of a small sphere colliding with a large sphere suggests a convenient method of definition when dealing with ions moving in a gas. When a small sphere collides with a large sphere, and both are perfectly elastic and perfectly smooth, then all directions of motion of the small sphere, after collision, are equally probable. It may therefore be supposed that collisions between the molecules and the ions are such that all directions of motion of the molecule are equally probable after collision. Hence, if l' be the mean free path of a molecule when moving in a gas containing N molecules per cubic centimetre of particles of the same mass and size as the ions, then

$$K = \tfrac{1}{3}l'V' = \tfrac{1}{3}(l+\lambda)V,$$

V' being the velocity of agitation of the molecule. The number of collisions per second C between the molecule and the particles, or ions, when there are N of them per cubic centimetre, is equal to the number of collisions per second between an ion and the molecules of the gas, when the latter contains N molecules per cubic centimetre. Hence,

$$l/l' = V/V' \quad \text{and} \quad lV'^2 = (l+\lambda)V^2 \quad \text{or} \quad \frac{l+\lambda}{l} = \frac{V'^2}{V^2} = \frac{m}{m'},$$

where m is the mass of an ion and m' that of a molecule.

Hence $K = \frac{1}{3}LV$ and $U = \frac{Xe}{m}\frac{L}{V}$, where $L = l + \lambda = \frac{lm}{m'}$,

L being the average distance that an ion will travel in the gas when it is projected with a velocity V in a given direction, m the mass of the ion, and m' that of a molecule of the gas, l the mean free path of an ion between collisions with molecules, these collisions being supposed to be of such a nature that all directions of motion are equally probable for the molecule after colliding.

9. Since the mean velocity of ions due to diffusion from places of high density to those of low density is $-K/n \, . \, dn/dx$, the velocity u when an electric force is also acting, is given by the equation

$$u = -\frac{K}{n}\frac{dn}{dx} + \frac{Xe}{m}\frac{L}{V}.$$

Hence $$\frac{1}{K} nu = -\frac{dn}{dx} + \frac{3nXe}{mV^2} \quad \text{or} \quad \frac{1}{K}(pu) = -\frac{dp}{dx} + nXe,$$

since p, the partial pressure of the ions, is $\frac{1}{3}mnV^2$.

This equation, and two similar equations for the y and z directions, are the well-known general equations of motion of particles through a gas, and the above investigations show that they follow immediately from the expressions for the rate of diffusion and the velocity under an electric force, even when *very* improbable assumptions are made with regard to the collisions as shown in section 6, provided that the same assumptions are made in calculating the two quantities that are involved.

On the Propagation of Waves through a Stratified Medium, with Special Reference to the Question of Reflection.

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The medium is supposed to be such that its properties are everywhere a function of but one co-ordinate x, being of one uniform quality where x is less than a certain value x_1, and of another uniform quality (in general, different from the first) where x exceeds a greater value x_{m-1}; and the principal problem is the investigation of the reflection which in general ensues when plane waves in the first medium are incident upon the stratifications. For the present we suppose the quality to be uniform through strata of finite thickness, the first transition occurring when $x = x_1$, the second at $x = x_2$, and the last at $x = x_{m-1}$.

The expressions for the waves in the various media in order may be taken to be

$$\phi_1 = \mathrm{A}_1 e^{i[ct+by-a_1(x-x_1)]} + \mathrm{B}_1 e^{i[ct+by+a_1(x-x_1)]}, \tag{1}$$

$$\phi_2 = \mathrm{A}_2 e^{i[ct+by-a_2(x-x_1)]} + \mathrm{B}_2 e^{i[ct+by+a_2(x-x_1)]},$$

$$\phi_3 = \mathrm{A}_3 e^{i[ct+by-a_3(x-x_2)]} + \mathrm{B}_3 e^{i[ct+by+a_3(x-x_2)]},$$

and so on, the A's and B's denoting arbitrary constants. The first terms represent the waves travelling in the positive direction, the second those travelling in the negative direction; and our principal aim is the determination of the ratio $\mathrm{B}_1/\mathrm{A}_1$ imposed by the conditions of the problem, including the requirement that in the final medium there shall be no negative wave.

As in the simple transition from one uniform medium to another ('Theory of Sound,' § 270), the symbols c and b are common to all the media, the first depending merely upon the periodicity, while the constancy of the second is required in order that the traces of the various waves on the surfaces of transition should move together—equivalent to the ordinary law of refraction. In the usual optical notation, if V be the velocity of propagation and θ the angle of incidence,

$$c = 2\pi\mathrm{V}/\lambda, \qquad b = (2\pi/\lambda)\sin\theta, \qquad a = (2\pi/\lambda)\cos\theta, \tag{2}$$

where V/λ, $\lambda^{-1}\sin\theta$ are the same in all the strata. On the other hand a is variable and is connected with the direction of propagation within the stratum by the relation

$$a = b\cot\theta. \tag{3}$$

The a's are thus known in terms of the original angle of incidence and of the various refractive indices.

Since the factor $e^{i(ct+by)}$ runs through all our expressions, we may regard it as understood and write simply

$$\phi_1 = A_1 e^{-ia_1(x-x_1)} + B_1 e^{ia_1(x-x_1)}, \tag{4}$$

$$\phi_2 = A_2 e^{-ia_2(x-x_1)} + B_2 e^{ia_2(x-x_1)}, \tag{5}$$

$$\phi_3 = A_3 e^{-ia_3(x-x_2)} + B_3 e^{ia_3(x-x_2)}, \tag{6}$$

. . . .

$$\phi_m = A_m e^{-ia_m(x-x_{m-1})} + B_m e^{ia_m(x-x_{m-1})}. \tag{7}$$

In the problem of reflection we are to make $B_m = 0$, and (if we please) $A_m = 1$.

We have now to consider the boundary conditions which hold at the surfaces of transition. In the case of sound travelling through gas, where ϕ is taken to represent the velocity-potential, these conditions are the continuity of $d\phi/dx$ and of $\sigma\phi$, where σ is the density. Whether the multiplier attaches to the dependent variable itself or to its derivative is of no particular significance. For example, if we take a new dependent variable ψ, equal to $\sigma\phi$, the above conditions are equivalent to the continuity of ψ and of $\sigma^{-1}d\psi/dx$. Nor should we really gain generality by introducing a multiplier in both places. We may therefore for the present confine ourselves to the acoustical form, knowing that the results will admit of interpretation in numerous other cases.

At the first transition $x = x_1$ the boundary conditions give

$$a_1(B_1 - A_1) = a_2(B_2 - A_2), \qquad \sigma_1(B_1 + A_1) = \sigma_2(B_2 + A_2). \tag{8}$$

If we stop here, we have the simple case of the juxtaposition of two media both of infinite depth. Supposing $B_2 = 0$, we get

$$\frac{B_1}{A_1} = \frac{\sigma_2/\sigma_1 - a_2/a_1}{\sigma_2/\sigma_1 + a_2/a_1} = \frac{\sigma_2/\sigma_1 - \cot\theta_2/\cot\theta_1}{\sigma_2/\sigma_1 + \cot\theta_2/\cot\theta_1}. \tag{9}$$

For a further discussion of (9) reference may be made to 'Theory of Sound' (*loc. cit.*). In the case of the simple gases the compressibilities are the same, and $\sigma_1 \sin^2\theta_1 = \sigma_2 \sin^2\theta_2$. The general formula (9) then identifies itself with Fresnel's expression

$$\frac{\tan(\theta_1 - \theta_2)}{\tan(\theta_1 + \theta_2)}. \tag{10}$$

On the other hand, if $\sigma_2 = \sigma_1$, the change being one of compressibility only, we find

$$(9) = \frac{\sin(\theta_2 - \theta_1)}{\sin(\theta_2 + \theta_1)}, \tag{11}$$

Fresnel's other expression.

In the above it is supposed that a_2 (and θ_2) are real. If the wave be incident in the more refractive medium and the angle of incidence be too great, a_2 becomes imaginary, say $-ia_2'$. In this case, of course, the reflection is total, the modulus of (9) becoming unity. The change of phase incurred is given by (9). In accordance with what has been said these results are at once available for the corresponding optical problems.

If there are more than two media, the boundary conditions at $x = x_2$ are—

$$a_2\left\{B_2e^{ia_2(x_2-x_1)}-A_2e^{-ia_2(x_2-x_1)}\right\} = a_3(B_3-A_3), \tag{12}$$

$$\sigma_2\left\{B_2e^{ia_2(x_2-x_1)}+A_2e^{-ia_2(x_2-x_1)}\right\} = \sigma_3(B_3+A_3), \tag{13}$$

and so on. For extended calculations it is desirable to write these equations in an abbreviated shape. We set

$$B_2-A_2 = H_2, \qquad B_2+A_2 = K_2, \quad \text{etc.}, \tag{14}$$

$$\cos a_2(x_2-x_1) = c_1, \qquad i\sin a_2(x_2-x_1) = s_1, \quad \text{etc.} \tag{15}$$

$$a_3/a_2 = \alpha_2, \qquad \sigma_3/\sigma_2 = \beta_2, \quad \text{etc.}; \tag{16}$$

and the series of equations then takes the form

$$H_1 = \alpha_1 H_2, \qquad K_1 = \beta_1 K_2, \tag{17}$$

$$c_1H_2+s_1K_2 = \alpha_2H_3, \qquad s_1H_2+c_1K_2 = \beta_2K_3, \tag{18}$$

$$c_2H_3+s_2K_3 = \alpha_3H_4, \qquad s_2H_3+c_2K_3 = \beta_3K_4, \tag{19}$$

and so on. In the reflection problem the special condition is the numerical equality of H and K of highest suffix. We may make

$$H = -1, \qquad K = +1. \tag{20}$$

As we have to work backwards from the terms of highest suffix, it is convenient to solve algebraically each pair of simple equations. In this way, remembering that $c^2-s^2 = 1$, we get

$$H_1 = \alpha_1H_2, \qquad K_1 = \beta_1K_2, \tag{21}$$

$$H_2 = c_1\alpha_2H_3-s_1\beta_2K_3, \qquad K_2 = -s_1\alpha_2H_3+c_1\beta_2K_3, \tag{22}$$

$$H_3 = c_2\alpha_3H_4-s_2\beta_3K_4, \qquad K_3 = -s_2\alpha_3H_4+c_2\beta_3K_4, \tag{23}$$

and so on. In these equations the c's and the β's are real, and also the α's, unless there is "total reflection"; the s's are pure imaginaries, with the same reservation.

When there are three media, we are to suppose in the problem of reflection that $H_3 = -1$, $K_3 = 1$. Thus from (21), (22),

$$H_1 = -\alpha_1(c_1\alpha_2+s_1\beta_2), \qquad K_1 = \beta_1(s_1\alpha_2+c_1\beta_2);$$

so that

$$\frac{B_1}{A_1} = \frac{K_1+H_1}{K_1-H_1} = \frac{c_1(\beta_1\beta_2-\alpha_1\alpha_2)+s_1(\alpha_2\beta_1-\alpha_1\beta_2)}{c_1(\beta_1\beta_2+\alpha_1\alpha_2)+s_1(\alpha_2\beta_1+\alpha_1\beta_2)}. \tag{24}$$

If there be no "total reflection," the relative intensity of the reflected waves is

$$\frac{c_1^2(\beta_1\beta_2-\alpha_1\alpha_2)^2-s_1^2(\alpha_2\beta_1-\alpha_1\beta_2)^2}{c_1^2(\beta_1\beta_2+\alpha_1\alpha_2)^2-s_1^2(\alpha_2\beta_1+\alpha_1\beta_2)^2}, \tag{25}$$

where $$c_1^2=\cos^2 a_2(x_2-x_1), \qquad -s_1^2=\sin^2 a_2(x_2-x_1). \tag{26}$$

The reflection will vanish independently of the values of c_1 and s_1, *i.e.*, whatever may be the thickness of the middle layer, provided

$$\beta_1\beta_2-\alpha_1\alpha_2=0, \quad \alpha_2\beta_1-\alpha_1\beta_2=0; \quad \text{or} \quad \beta_1=\alpha_1, \quad \beta_2=\alpha_2,$$

since these quantities are all positive. Reference to (9) shows that these are the conditions of vanishing reflection at the two surfaces of transition considered separately.

If these conditions be not satisfied, the evanescence of (25) requires that either c_1 or s_1 be zero. The latter case is realised if the intermediate layer be abolished, and the remaining condition is equivalent to $\sigma_3/\sigma_1=a_3/a_1$, as was to be expected from (9). We learn now that, if there would be no reflection in the absence of an intermediate layer, its introduction will have no effect provided $a_2(x_2-x_1)$ be a multiple of π. An obvious example is when the first and third media are similar, as in the usual theory of "thin plates."

On the other hand, if c_1, or $\cos a_2(x_2-x_1)$, vanish, the remaining requirement for the evanescence of (25) is that $\beta_2/\alpha_2=\beta_1/\alpha_1$.

In this case $$\frac{\beta_1-\alpha_1}{\beta_1+\alpha_1}=\frac{\beta_2-\alpha_2}{\beta_2+\alpha_2};$$

so that by (9) the reflections at the two faces are equal in all respects.

In general, if the third and first media are similar, (25) reduces to

$$\frac{\{\beta_1/\alpha_1-\alpha_1/\beta_1\}^2\sin^2 a_2(x_2-x_1)}{4\cos^2 a_2(x_2-x_1)+\{\beta_1/\alpha_1+\alpha_1/\beta_1\}^2\sin^2 a_2(x_2-x_1)}, \tag{27}$$

which may readily be identified with the expression usually given in terms of (9).

It remains to consider the cases of so-called total reflection. If this occurs only at the *second* surface of transition, a_1, a_2 are real, while a_3 is a pure imaginary. Thus α_1 is real, and α_2 is imaginary; c_1 is real always, and s_1 is imaginary as before; the β's are always real. Thus, if we separate the real and imaginary parts of the numerator and denominator of (24), we get

$$\frac{B_1}{A_1}=\frac{c_1\beta_1\beta_2+s_1\alpha_2\beta_1-c_1\alpha_1\alpha_2-s_1\alpha_1\beta_2}{c_1\beta_1\beta_2+s_1\alpha_2\beta_1+c_1\alpha_1\alpha_2+s_1\alpha_1\beta_2}, \tag{28}$$

of which the modulus is unity. In this case, accordingly, the reflection back in the first medium is literally total, whatever may be the thickness of the intermediate layer, as was to be expected.

The separation of real and imaginary parts follows the same rule when a_2 is imaginary, as well as a_3. For then α_1 is imaginary, while α_2, s_1 are real. Thus $s_1\alpha_2\beta_1$ remains real, and $c_1\alpha_1\alpha_2$, $s_1\alpha_1\beta_2$ remain imaginary. The reflection back in the first medium is total in this case also.

The only other case requiring consideration occurs when a_2 is imaginary and a_3 real. The reflection is then total if the middle layer be thick enough, but if this thickness be reduced, the reflection cannot remain total, as is evident if we suppose the thickness to vanish. The ratios α_1, α_2 are now both imaginary, while s_1 is real. The separation of real and imaginary parts stands as in (24), and the intensity of reflection is still expressed by (25). If we take $a_2 = -ia_2'$, we may write in place of (25),

$$\frac{(\beta_1\beta_2-\alpha_1\alpha_2)^2\cosh^2 a_2'(x_2-x_1)-(\alpha_2\beta_1-\alpha_1\beta_2)^2\sinh^2 a_2'(x_2-x_1)}{(\beta_1\beta_2+\alpha_1\alpha_2)^2\cosh^2 a_2'(x_2-x_1)-(\alpha_2\beta_1+\alpha_1\beta_2)^2\sinh^2 a_2'(x_2-x_1)}. \tag{29}$$

When x_2-x_1 is extremely small, this reduces to

$$\frac{(\beta_1\beta_2-\alpha_1\alpha_2)^2}{(\beta_1\beta_2+\alpha_1\alpha_2)^2}, \quad \text{or} \quad \frac{(\sigma_3/\sigma_1-a_3/a_1)^2}{(\sigma_3/\sigma_1+a_3/a_1)^2},$$

in accordance with (9).

When on the other hand x_2-x_1 exceeds a few wave-lengths, (29) approaches unity, as we see from a form, equivalent to (29), viz.,

$$\frac{(\beta_1^2-\alpha_1^2)(\beta_2^2-\alpha_2^2)\cosh^2 a_2'(x_2-x_1)+(\alpha_2\beta_1-\alpha_1\beta_2)^2}{(\beta_1^2-\alpha_1^2)(\beta_2^2-\alpha_2^2)\cosh^2 a_2'(x_2-x_1)+(\alpha_2\beta_1+\alpha_1\beta_2)^2}. \tag{30}$$

It is to be remembered that in (30), α_1^2, α_2^2, $\alpha_1\alpha_2$ have negative values.

The form assumed when the third medium is similar to the first may be noted. In this case $\alpha_1\alpha_2 = 1$, $\beta_1\beta_2 = 1$, and we get from (29)

$$\frac{(\beta_1/\alpha_1-\alpha_1/\beta_1)^2\sinh^2 a_2'(x_2-x_1)}{(\beta_1/\alpha_1-\alpha_1/\beta_1)^2\sinh^2 a_2'(x_2-x_1)-4}. \tag{31}$$

In this case, of course, the reflection vanishes when x_2-x_1 is sufficiently reduced.

Equations (21), etc., may be regarded as constituting the solution of the general problem. If there are m media, we suppose $H_m = -1$, $K_m = 1$, thence calculate in order from the pairs of simple equations H_{m-1}, K_{m-1}; H_{m-2}, K_{m-2}, etc., until H_1 and K_1 are reached; and then determine the ratio B_1/A_1. The procedure would entail no difficulty in any special case numerically given; but the algebraic expression of H_1 and K_1 in terms of H_m and K_m soon becomes complicated, unless further simplifying conditions are introduced. Such simplification may be of two kinds. In the first it is supposed that the total thickness between the initial and final media is small relatively to the wave-lengths, so that the phase-changes occurring within the layer are of subordinate importance. In the second kind of simplification the thicknesses are left arbitrary, but the changes in the character of the medium, which occur at each transition, are supposed small.

The problem of a thin transitional layer has been treated by several authors, L. Lorenz,* Van Ryn,† Drude,‡ Schott,§ and Maclaurin.‖ A full account will be found in 'Theory of Light' by the last named. It will therefore not be necessary to treat the subject in detail here; but it may be worth while to indicate how the results may be derived from our equations. For this purpose it is convenient to revert to the original notation so far as to retain a and σ. Thus in place of (17), etc., we write

$$a_1 H_1 = a_2 H_2, \qquad \sigma_1 K_1 = \sigma_2 K_2. \tag{32}$$

$$a_2(c_1 H_2 + s_1 K_2) = a_3 H_3, \qquad \sigma_2(s_1 H_2 + c_1 K_2) = \sigma_3 K_3, \quad \text{etc.} \tag{33}$$

In virtue of the supposition that all the layers are thin, the c's are nearly equal to unity and the s's are small. Thus, for a first approximation we identify c with 1 and neglect s altogether, so obtaining

$$a_1 H_1 = a_2 H_2 = \ldots = a_m H_m, \qquad \sigma_1 K_1 = \sigma_2 K_2 = \ldots = \sigma_m K_m. \tag{34}$$

The relation of H_1, K_1 to H_m, K_m is the same as if the transition between the extreme values took place without intermediate layers, and the law of reflection is not disturbed by the presence of these layers, as was to be expected.

For the second approximation we may still identify the c's with unity, while the s's are retained as quantities of the first order. Adding together the column of equations constituting the first members of (32), (33), etc., we find

$$a_1 H_1 + a_2 s_1 K_2 + a_3 s_2 K_3 + \ldots + a_{m-1} s_{m-2} K_{m-1} = a_m H_m; \tag{35}$$

and in like manner, with substitution of σ for a and interchange of K and H,

$$\sigma_1 K_1 + \sigma_2 s_1 H_2 + \ldots + \sigma_{m-1} s_{m-2} H_{m-1} = \sigma_m K_m. \tag{36}$$

In the small terms containing s's we may substitute the approximate values of H and K from (34). For the problem of reflection we suppose $H_m + K_m = 0$. Hence

$$\frac{H_1}{K_1} = -\frac{\sigma_1 a_m}{\sigma_m a_1} \frac{1 + \dfrac{\sigma_m}{a_m} \Sigma \dfrac{a_2 s_1}{\sigma_2}}{1 + \dfrac{a_m}{\sigma_m} \Sigma \dfrac{\sigma_2 s_1}{a_2}}. \tag{37}$$

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* 'Pogg. Ann.,' 1860, vol. 111, p. 460.

† 'Wied. Ann.,' 1883, vol. 20, p. 22.

‡ 'Wied. Ann.,' 1891, vol. 43, p. 126.

§ 'Phil. Trans.,' 1894, vol. 185, p. 823.

‖ 'Roy. Soc. Proc.,' A, 1905, vol. 76, p. 49.

In (37) $s_1 = ia_2(x_2 - x_1)$, and so on, so that

$$\Sigma \frac{a_2 s_1}{\sigma_1} = i\int \frac{a^2\,dx}{\sigma}, \qquad \Sigma \frac{\sigma_2 s_1}{a_2} = i\int \sigma\,dx, \tag{38}$$

the integration extending over the layer of transition.

One conclusion may be drawn at once. To this degree of approximation the reflection is independent of the order of the strata. It will be noted that the sums in (37) are pure imaginaries. In what follows we shall suppose that a_m is real.

As the final result for the reflection, we find

$$\frac{B_1}{A_1} = \frac{K_1 + H_1}{K_1 - H_1} = Re^{i\delta}, \tag{39}$$

where

$$R = \frac{\sigma_m/\sigma_1 - a_m/a_1}{\sigma_m/\sigma_1 + a_m/a_1}, \tag{40}$$

$$\tan\delta = 2\,\frac{\dfrac{a_m}{\sigma_m}\displaystyle\int \sigma\,dx - \dfrac{\sigma_m}{a_m}\displaystyle\int \frac{a^2\,dx}{\sigma}}{\dfrac{a_1\sigma_m}{a_m\sigma_1} - \dfrac{a_m\sigma_1}{a_1\sigma_m}}. \tag{41}$$

To this order of approximation the *intensity* of the reflection is unchanged by the presence of the intermediate layers, unless, indeed, the circumstances are such that (40) is itself small. If $\sigma_m/\sigma_1 = a_m/a_1$ absolutely, we have

$$R = \tfrac{1}{2}\left\{\frac{a_m}{\sigma_m}\int \sigma\,dx - \frac{\sigma_m}{a_m}\int \frac{a^2\,dx}{\sigma}\right\} \tag{42}$$

and $\delta = \frac{1}{2}\pi$. This case is important in Optics, as representing the reflection at the polarising angle from a contaminated surface.

The two important optical cases: (i) where σ is constant, leading (when there is no transitional layer) to Fresnel's formula (11), and (ii) where $\sigma\sin^2\theta$ is constant, leading to (10), are now easily tretaed as special examples. Introducing the refractive index μ, we find after reduction for case (i)

$$\delta' = -\frac{4\pi\cos\theta_1}{\lambda_1(\mu_m^2 - \mu_1^2)}\int (\mu_m^2 - \mu^2)\,dx, \tag{43}$$

where λ_1, μ_1, relate to the first medium, μ_m is the index for the last medium, and the integration is over the layer of transition. The application of (43) should be noticed when the layer is in effect abolished, either by supposing $\mu = \mu_m$, or, on the other hand, $\mu = \mu_1$.

In the second case (42), corresponding to the polarising angle, becomes

$$R = \frac{\pi}{\lambda_1\mu_1\sqrt{(\mu_m^2 + \mu_1^2)}}\int \frac{(\mu^2 - \mu_1^2)(\mu^2 - \mu_m^2)}{\mu^2}\,dx. \tag{44}$$

In general for this case

$$\delta'' = -\frac{4\pi\cos\theta_1}{\lambda_1}\frac{\cos^2\theta_1\int(\mu_m{}^2-\mu^2)\,dx-\sin^2\theta_1\int(\mu_m{}^2-\mu^2)\left(\frac{\mu_1{}^2}{\mu^2}+\frac{\mu_1{}^2}{\mu_m{}^2}-1\right)dx}{(\mu_m{}^2-\mu_1{}^2)\left(\cos^2\theta_1-\frac{\mu_1{}^2}{\mu_m{}^2}\sin^2\theta_1\right)}. \tag{45}$$

The second fraction in (45) is equal to the thickness of the layer of transition simply, when we suppose $\mu = \mu_1$.

Further, $$\delta''-\delta' = -\frac{4\pi}{\lambda_1}\frac{\cos\theta_1\sin^2\theta_1}{\mu_m{}^2-\mu_1{}^2}\frac{\int\frac{(\mu_m{}^2-\mu^2)(\mu^2-\mu_1{}^2)}{\mu}dx}{\cos^2\theta_1-\frac{\mu_1{}^2}{\mu_m{}^2}\sin^2\theta_1}, \tag{46}$$

the difference of phase vanishing, as it ought to do, when $\mu = \mu_1$, or μ_m, or, again, when $\theta_1 = 0$.

It should not escape notice that the expressions (10) and (11) have different signs when θ_1 and θ_2 are small. This anomaly, as it must appear from an optical point of view, should be corrected when we consider the significance of $\delta''-\delta'$. The origin of it lies in the circumstance that, in our application of the boundary conditions, we have, in effect, used different vectors as dependent variables to express light of the two polarisations. For further explanation reference may be made to former writings, *e.g.* "On the Dynamical Theory of Gratings."*

If throughout the range of integration, μ is intermediate between the terminal values μ_1, μ_m, the reflection is of the kind called positive by Jamin. The transition may well be of this character when there is no contamination. On the other hand, the reflection is negative, if μ has throughout a value outside the range between μ_1 and μ_m. It is probable that something of this kind occurs when water has a greasy surface.

The formulæ required in Optics, viz. (43), (44), (45), (46), are due, in substance, to Lorenz and van Ryn. The more general expressions (41), (42), do not seem to have been given.

There is no particular difficulty in pursuing the approximation from (32), etc. At the next stage the second term in the expansion of the c's must be retained, while the s's are still sufficiently represented by the first terms. The result, analogous to (37), (38), is

$$\frac{\mathrm{H}_1}{\mathrm{K}_1} = -\frac{\sigma_1 a_m}{\sigma_m a_1}\frac{1-\int_0^d\sigma\,.\int_0^x\frac{a^2\,dx}{\sigma}\,.\,dx+i\frac{\sigma_m}{a_m}\int_0^d\frac{a^2}{\sigma}dx}{1-\int_0^d\frac{a^2}{\sigma}\,.\int_0^x\sigma\,dx\,.\,dx+i\frac{a_m}{\sigma_m}\int_0^d\sigma\,dx}, \tag{47}$$

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* 'Roy. Soc. Proc.,' A, 1907, vol. 79, p. 413.

in which the terminal abscissæ of the variable layer are taken to be 0 and d, instead of x_1 and x_{m-1}. I do not follow out the application to particular cases such as $\sigma =$ constant, or $\sigma \sin^2\theta =$ constant. For this reference may be made to Maclaurin, who, however, uses a different method.

The second case which allows of a simple approximate expression for the reflection arises when all the partial reflections are small. It is then hardly necessary to appeal to the general equations: the method usually employed in optics suffices. The assumptions are that at each surface of transition the incident waves may be taken to be the same as in the first medium, merely retarded by the appropriate amount, and that each partial reflection reaches the first medium no otherwise modified than by such retardation. This amounts to the neglect of waves three times reflected. Thus

$$\frac{\mathrm{B}_1}{\mathrm{A}_1} = \frac{\beta_1-\alpha_1}{\beta_1+\alpha_1} + \frac{\beta_2-\alpha_2}{\beta_2+\alpha_2} e^{-2ia_2(x_2-x_1)} + \frac{\beta_3-\alpha_3}{\beta_3+\alpha_3} e^{-2i[a_2(x_2-x_1)+a_3(x_3-x_2)]} + \dots \tag{48}$$

An interesting question suggests itself as to the manner in which the transition from one uniform medium to another must be effected in order to obviate reflection, and especially as to the least thickness of the layer of transition consistent with this result. If there be two transitions only, the least thickness of the layer is obtained by supposing in (48)

$$\frac{\beta_1-\alpha_1}{\beta_1+\alpha_1} = \frac{\beta_2-\alpha_2}{\beta_2+\alpha_2} \tag{49}$$

and

$$2a_2(x_2-x_1) = \pi; \tag{50}$$

and this conclusion, as we have seen already, is not limited to the case of small differences of quality. In its application to perpendicular incidence, (50) expresses that the thickness of the layer is one-quarter of the wave-length proper to the layer. The two partial reflections are equal in magnitude and sign. It is evident that nothing better than this can be done so long as the reflections are of one sign, however numerous the surfaces of transition may be.

If we allow the partial reflections to be of different signs, some reduction of the necessary thickness is possible. For example, suppose that there are two intermediate layers of equal thickness, of which the first is similar to the final uniform medium, and the second similar to the initial uniform medium. Of the three partial reflections the first and third are similar, but the second is of the opposite sign. If three vectors of equal numerical value compensate one another, they must be at angles of 120°. The necessary conditions are satisfied (in the case of perpendicular transmission) if the total thickness ($2l$) is $\frac{1}{6}\lambda$, in accordance with

$$1 - e^{-4\pi il/\lambda} + e^{-8\pi il/\lambda} = 0.$$

The total thickness of the layer of transition is thus somewhat reduced, but only by a very artificial arrangement, such as would not usually be contemplated when a layer of transition is spoken of. If the progress from the first to the second uniform quality be always *in one direction*, reflection cannot be obviated unless the layer be at least $\frac{1}{4}\lambda$ thick.

The general formula (48) may be adapted to express the result appropriate to continuous variation of the medium. Suppose, for example, that σ is constant, making $\beta = 1$, and corresponding to the continuity of both ϕ and $d\phi/dx$.* It is convenient to suppose that the variation commences at $x = 0$. Then (48) may be written

$$\frac{B_1}{A_1} = -\int \frac{da}{2a} e^{-2i\int_0^x a\,dx}, \tag{51}$$

a at any point x being connected with the angle of propagation by the usual relation (3). In the special case of perpendicular propagation, $a = 2\pi\mu/\lambda_1\mu_1$, μ being refractive index and λ_1, μ_1 relating to the first medium.

A curious example, theoretically possible even if unrealisable in experiment, arises when the variable medium is constituted in such a manner that the velocity of propagation is everywhere constant, so that there is no refraction. Then a is constant, $\alpha = 1$, and (48) gives

$$\frac{B_1}{A_1} = \int \frac{d\sigma}{2\sigma} e^{-2iax}. \tag{52}$$

Some of the questions relating to the propagation of waves in a variable medium are more readily treated on the basis of the appropriate differential equation. As in (1), we suppose that the waves are plane, and that the medium is stratified in plane strata perpendicular to x, and we usually omit the exponential factors involving t and y, which may be supposed to run through. In the case of perpendicular propagation, y would not appear at all.

Consider the differential equation

$$\frac{d^2\phi}{dx^2} + \kappa^2\phi = 0, \tag{53}$$

in which (unless κ^2 can be infinite) it is necessary to suppose that ϕ and $d\phi/dx$ are continuous; κ^2 is a function of x, which must be everywhere positive when the transmission is perpendicular, as, for example, in the case of a stretched string. When the transmission is oblique to the strata,

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* These would be the conditions appropriate to a stretched string of variable longitudinal density vibrating transversely.

κ^2 may become negative, corresponding to "total reflection," but in most of what follows we shall assume that this does not happen. The continuity of ϕ and $d\phi/dx$, even though κ^2 be discontinuous, appears to limit the application of (53) to certain kinds of waves, although, as a matter of analysis, the general differential equation of the second order may always be reduced to this form.*

In the theory of a uniform medium, we may consider stationary waves or progressive waves. The former may be either

$$\phi = \mathrm{A}\cos\kappa_0 x\cos pt, \quad \text{or} \quad \phi = \mathrm{B}\sin\kappa_0 x\sin pt;$$

and, if $\mathrm{B} = \pm\mathrm{A}$, the two may be combined, so as to constitute progressive waves

$$\phi = \mathrm{A}\cos(pt\pm\kappa_0 x).$$

Conversely, progressive waves, travelling in opposite directions, may be combined so as to constitute stationary waves. When we pass to variable media, no ambiguity arises respecting stationary waves; they are such that the phase is the same at all points. But is there such a thing as a progressive wave? In the full sense of the phrase there is not. In general, if we contemplate the wave forms at two different times, the difference between them cannot be represented by a mere shift of position proportional to the interval of time which has elapsed.

The solution of (53) may be taken to be

$$\phi = \mathrm{A}'\psi(x)+\mathrm{B}'\chi(x), \tag{54}$$

where $\psi(x)$, $\chi(x)$, are real oscillatory functions of x; A', B', arbitrary constants as regards x. If we introduce the time-factor, writing p in place of the less familiar c of (1), we may take

$$\phi = \mathrm{A}\cos pt\,.\,\psi(x)+\mathrm{B}\sin pt\,.\,\chi(x); \tag{55}$$

and this may be put into the form

$$\phi = \mathrm{H}\cos(pt-\theta), \tag{56}$$

where
$$\mathrm{H}\cos\theta = \mathrm{A}\psi(x), \qquad \mathrm{H}\sin\theta = \mathrm{B}\chi(x), \tag{57}$$

or
$$\mathrm{H}^2 = \mathrm{A}^2[\psi(x)]^2+\mathrm{B}^2[\chi(x)]^2, \tag{58}$$

$$\theta = \tan^{-1}\frac{\mathrm{B}\,.\,\chi(x)}{\mathrm{A}\,.\,\psi(x)}. \tag{59}$$

But the expression for ϕ in (56) cannot be said to represent in general a progressive wave. We may illustrate this even from the case of the uniform medium where $\psi(x) = \cos\kappa x$, $\chi(x) = \sin\kappa x$. In this case (56) becomes

$$\phi = \{\mathrm{A}^2\cos^2\kappa x+\mathrm{B}^2\sin^2\kappa x\}^{\frac{1}{2}}\cos\left\{pt-\tan^{-1}\left(\frac{\mathrm{B}}{\mathrm{A}}\tan\kappa x\right)\right\}. \tag{60}$$

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* Forsyth's 'Differential Equations,' § 59.

If $B = \pm A$, reduction ensues to the familiar positive or negative progressive wave. But if B be not equal to $\pm A$, (55), taking the form

$$\phi = \tfrac{1}{2}(A+B)\cos(pt-\kappa x)+\tfrac{1}{2}(A-B)\cos(pt+\kappa x),$$

clearly does not represent a progressive wave. The mere possibility of reduction to the form (57) proves little, without an examination of the character of H and θ.

It may be of interest to consider for a moment the character of θ in (60). If B/A, or, say, m, is positive, θ may be identified with κx at the quadrants, but elsewhere they differ, unless $m = 1$. Introducing the imaginary expressions for tangents, we find

$$\theta = \kappa x + M\sin 2\kappa x + \tfrac{1}{2}M^2\sin 4\kappa x + \tfrac{1}{3}M^3\sin 6\kappa x + \ldots, \tag{61}$$

where
$$M = \frac{m-1}{m+1}. \tag{62}$$

When κ is constant, one of the solutions of (53) makes ϕ proportional to $e^{-i\kappa x}$. Acting on this suggestion, and following out optical ideas, let us assume in general

$$\phi = \eta e^{-i\int a\,dx}, \tag{63}$$

where the amplitude η and a are real functions of x, which, for the purpose of approximations, may be supposed to vary slowly. Substituting in (53), we find

$$\frac{d^2\eta}{dx^2}+(\kappa^2-a^2)\,\eta-2ia^{\frac{1}{2}}\frac{d}{dx}(a^{\frac{1}{2}}\eta) = 0. \tag{64}$$

For a first approximation, we neglect $d^2\eta/dx^2$. Hence

$$\kappa = a, \qquad \kappa^{\frac{1}{2}}\eta = C, \tag{65}$$

so that
$$\phi = C\kappa^{-\frac{1}{2}}e^{ipt}e^{-i\int\kappa\,dx}, \tag{66}$$

or in real form,
$$\phi = C\kappa^{-\frac{1}{2}}\cos\left(pt-\int\kappa\,dx\right). \tag{67}$$

If we hold rigorously to the suppositions expressed in (65), the satisfaction of (64) requires that $d^2\eta/dx^2 = 0$, or $d^2\kappa^{-\frac{1}{2}}/dx^2 = 0$. With omission of arbitrary constants affecting merely the origin and the scale of x, this makes $\kappa^2 = x^{-4}$, corresponding to the differential equation

$$x^4\frac{d^2\phi}{dx^2}+\phi = 0, \tag{68}$$

whose accurate solution is accordingly

$$\phi = Cxe^{i(pt-1/x)}. \tag{69}$$

In (69) the imaginary part may be rejected. The solution (69) is, of course, easily verified. In all other cases (67) is only an approximation.

As an example, the case where $\kappa^2 = n^2/x^2$ may be referred to. Here $\int \kappa dx = n \log x - \epsilon$, and (67) gives

$$\phi = Cx^{\frac{1}{2}} \cos(pt - n\log x + \epsilon) \tag{70}$$

as an approximate solution. We shall see presently that a slight change makes it accurate.

Reverting to (64), we recognise that the first and second terms are real, while the third is imaginary. The satisfaction of the equation requires therefore that

$$a^{\frac{1}{2}}\eta = C, \tag{71}$$

and that

$$\kappa^2 = C^4\eta^{-4} - \frac{1}{\eta}\frac{d^2\eta}{dx^2}; \tag{72}$$

while (63) becomes

$$\phi = \eta e^{-iC^2\int \eta^{-2}dx}. \tag{73}$$

Let us examine in what cases η may take the form Dx^r. From (72),

$$\kappa^2 = C^4D^{-4}x^{-4r} - r(r-1)x^{-2}. \tag{74}$$

If $r = 0$, κ^2 is constant. If $r = 1$, $\kappa^2 = C^4D^{-4}x^{-4}$, already considered in (68). The only other case in which κ^2 is a simple power of x occurs when $r = \frac{1}{2}$, making

$$\kappa^2 = (C^4D^{-4} + \tfrac{1}{4})x^{-2} = n^2x^{-2} \text{ (say)}. \tag{75}$$

Here $\eta = Dx^{\frac{1}{2}}$, $C^2\int \eta^{-2}dx = C^2/D^2 . \log x - \epsilon$, and the realised form of (73) is

$$\phi = Dx^{\frac{1}{2}} \cos\{pt - \sqrt{(n^2 - \tfrac{1}{4})}\log x + \epsilon\}, \tag{76}$$

which is the exact form of the solution obtained by approximate methods in (70). For a discussion of (76) reference may be made to 'Theory of Sound,' second edition, § 148*b*.

The relation between a and η in (71) is the expression of the energy condition, as appears readily if we consider the application to waves along a stretched string. From (53), with restoration of e^{ipt},

$$\frac{d\phi}{dt} = e^{ipt}e^{-i\int a dx} . ip\eta, \qquad \frac{d\phi}{dx} = e^{ipt}e^{-i\int a dx}\left\{\frac{d\eta}{dx} - ia\eta\right\}.$$

If the common phase factors be omitted, the parts of $d\phi/dt$ and $d\phi/dx$ which are in the same phase are as $p\eta$ and $a\eta$, and thus the mean work transmitted at any place is as $a\eta^2$. Since there is no accumulation of energy between two places, $a\eta^2$ must be constant.

When the changes are gradual enough, a may be identified with κ, and then $\eta \propto \kappa^{-\frac{1}{2}}$, as represented in (67).

If we regard η as a given function of x, a follows when C has been chosen, and also κ^2 from (72). In the case of perpendicular propagation κ^2 cannot be *negative, but this is the only restriction.* When η is constant, κ^2 is constant; *and thus if we suppose η to pass from one constant value to another through a finite transitional layer, the transition is also from one uniform κ^2 to another; and (73) shows that there is no reflection back into the first medium.* If the terminal values of η and therefore of κ^2 be given, and the transitional layer be thick enough, it will always be possible, and that in an infinite number of ways, to avoid a negative κ^2, and thus to secure complete transmission without reflection back; but if with given terminal values the layer be too much reduced, κ^2 must become negative. In this case reflection cannot be obviated.

It may appear at first sight as if this argument proved too much, and that there should be no reflection in any case so long as κ^2 is positive throughout. But although a constant η requires a constant κ^2, it does not follow conversely that a constant κ^2 requires a constant η, and, in fact, this is not true. *One* solution of (72), when κ^2 is constant, certainly is $\eta^2 = \mathrm{C}^2/\kappa$; but the complete solution necessarily includes two arbitrary constants, of which C is not one. From (60) it may be anticipated that a solution of (72) may be

$$\eta^2 = \mathrm{A}^2\cos^2\kappa x+\mathrm{B}^2\sin^2\kappa x = \tfrac{1}{2}(\mathrm{A}^2+\mathrm{B}^2)+\tfrac{1}{2}(\mathrm{A}^2-\mathrm{B}^2)\cos 2\kappa x. \tag{77}$$

From this we find on differentiation

$$\eta^3\frac{d^2\eta}{dx^2}+\kappa^2\eta^4 = \kappa^2\mathrm{A}^2\mathrm{B}^2;$$

and thus (72) is satisfied, provided that

$$\kappa^2\mathrm{A}^2\mathrm{B}^2 = \mathrm{C}^2. \tag{78}$$

It appears then that (77) subject to (78) is a solution of (72). The second arbitrary constant evidently takes the form of an arbitrary addition to x, and η will not be constant unless $\mathrm{A}^2 = \mathrm{B}^2$.

On the supposition that η and a are slowly varying functions, the approximations of (65) may be pursued. We find

$$\eta = \mathrm{C}\kappa^{-\frac{1}{2}}\left\{1-\tfrac{1}{4}\kappa^{-\frac{3}{2}}\frac{d^2\kappa^{-\frac{1}{2}}}{dx^2}\right\}, \tag{79}$$

$$a = \kappa+\tfrac{1}{2}\kappa^{-\frac{1}{2}}\frac{d^2\kappa^{-\frac{1}{2}}}{dx^2}. \tag{80}$$

The retardation, as usually reckoned in optics, is $\int\kappa dx$. The additional retardation according to (80) is

$$\tfrac{1}{2}\int\kappa^{-\frac{1}{2}}\frac{d^2\kappa^{-\frac{1}{2}}}{dx^2}dx = \tfrac{1}{2}\left[\kappa^{-\frac{1}{2}}\frac{d\kappa^{-\frac{1}{2}}}{dx}\right]-\tfrac{1}{2}\int\left(\frac{d\kappa^{-\frac{1}{2}}}{dx}\right)^2dx.$$

As applied to the transition from one uniform medium to another, the retardation is *less* than according to the first approximation by

$$\tfrac{1}{2}\int\left(\frac{d\kappa^{-\frac{1}{2}}}{dx}\right)^2dx. \tag{81}$$

The supposition that η varies slowly excludes more than a very small reflection.

Equations (79), (80) may be tested on the particular case already referred to where $\kappa = n/x$. We get

$$\eta = \mathrm{C}n^{-\frac{1}{2}}x^{\frac{1}{2}}\left(1+\frac{1}{16n^2}\right), \qquad a = \frac{1}{x}\left(n-\frac{1}{8n}\right);$$

so that

$$\int a\,dx = \left(n-\frac{1}{8n}\right)\log x.$$

When n^{-4} is neglected in comparison with unity, $n-\frac{1}{8}n^{-1}$ may be identified with $\sqrt{(n^2-\frac{1}{4})}$.

Let us now consider what are the possibilities of avoiding reflection when the transition layer (x_2-x_1) between two uniform media is reduced. If η_1, κ_1; η_2, κ_2 are the terminal values, (72) requires that

$$\kappa_1^2 = \mathrm{C}^4\eta_1^{-4}, \qquad \kappa_2^2 = \mathrm{C}^4\eta_2^{-4}.$$

We will suppose that $\eta_2 > \eta_1$. If the transition from η_1 to η_2 be made too quickly, viz., in too short a space, $d^2\eta/dx^2$ will become somewhere so large as to render κ^2 negative. The same consideration shows that at the beginning of the layer of transition (x_1), $d\eta/dx$ must vanish. The quickest admissible rise of η will ensue when the curve of rise is such as to make κ^2 vanish. When η attains the second prescribed value η_2, it must suddenly become constant, notwithstanding that this makes κ^2 positively infinite.

From (72) it appears that the curve of rise thus defined satisfies

$$\frac{d^2\eta}{dx^2} = \mathrm{C}^4\eta^{-3}. \tag{82}$$

The solution of (82), subject to the conditions that $\eta = \eta_1$, $d\eta/dx = 0$, when $x = x_1$, is

$$\eta^2-\eta_1^2 = \mathrm{C}^4\eta_1^{-2}(x-x_1)^2 = \kappa_1^2\eta_1^2(x-x_1)^2. \tag{83}$$

Again, when $\eta = \eta_2$, $x = x_2$, so that

$$\kappa_1^2(x_2-x_1)^2 = \frac{\eta_2^2-\eta_1^2}{\eta_1^2} = \frac{\kappa_1-\kappa_2}{\kappa_2}, \tag{84}$$

giving the minimum thickness of the layer of transition.

It will be observed that the minimum thickness of the layer of transition necessary to avoid reflection diminishes without limit with $\kappa_1-\kappa_2$, that is, as the difference between the two media diminishes. However, the arrangement under discussion is very artificial. In the case of the string, for example, it is supposed that the density drops suddenly from the first uniform value to zero, at which it remains constant for a time. At the end of this it becomes momentarily infinite, before assuming the second uniform value. The infinite longitudinal density at x_2 is equivalent to a finite load there attached. In the layer of transition, if so it may be called, the string remains straight during the passage of the waves.

If, as in the more ordinary use of the term, we require the transition to be such that κ^2 moves always in one direction from the first terminal value to the second, the problem is one already considered. The minimum thickness is such that κ^2 has throughout it a constant intermediate value, so chosen as to make the reflections equal at the two faces.

It would be of interest to consider a particular case in which κ^2 varies continuously and always in the one direction. As appears at once from (72), $d^2\eta/dx^2$, as well as $d\eta/dx$, must vanish at both ends of the layer, and there must also be a third point of inflection between. If the layer be from $x = 0$ to $x = \beta$, we may take

$$\frac{d^2\eta}{dx^2} = \mathrm{A}x(x-\alpha)(x-\beta). \tag{85}$$

We find that $\beta = 2\alpha$, and that

$$\frac{\eta-\eta_1}{\eta_2-\eta_1} = \frac{15x^3}{4\alpha^5}\left\{\frac{x^2}{20}-\frac{\alpha x}{4}+\frac{\alpha^2}{3}\right\}, \tag{86}$$

$$\frac{1}{\eta_2-\eta_1}\frac{d^2\eta}{dx^2} = \frac{15x}{4\alpha^5}(x-\alpha)(x-2\alpha). \tag{87}$$

From these κ^2 would have to be calculated by means of (72), and one question would be to find how far α might be reduced without interfering with the prescribed character of κ^2. But to discuss this in detail would lead us too far.

If the differences of quality in the variable medium are small, (72) simplifies. If η_0, κ_0 be corresponding values, subject to $\kappa_0^2 = \mathrm{C}^4\eta_0^{-4}$, we may take

$$\eta = \eta_0+\eta', \qquad \kappa^2 = \kappa_0^2+\delta\kappa^2, \tag{88}$$

where η' and $\delta\kappa^2$ are small, and (72) becomes approximately

$$\frac{d^2\eta'}{dx^2}+4\kappa_0^2\eta' = -\eta_0\delta\kappa^2. \tag{89}$$

Replacing x by t, representing *time*, we see that the problem is the same as that of a pendulum upon which displacing forces act; see 'Theory of Sound,' § 66. The analogue of the transition from one uniform medium to another is that of the pendulum initially at rest in the position of equilibrium, upon which at a certain time a displacing force acts. The force may be variable at first, but ultimately assumes a constant value. If there is to be no reflection in the original problem, the force must be of such a character that when it becomes constant the pendulum is left *at rest* in the new position. If the object be to effect the transition between the two states in the shortest possible time, but with forces which are restricted never to exceed the final value, it is pretty evident that the force must immediately assume the maximum admissible value, and retain it for such a time that the pendulum, then left free, will just reach the new position of equilibrium, after which the force is reimposed. The present solution is excluded, if it be required that the force never decrease in value. Under this restriction the best we can do is to make the force assume at once *half* its final value, and remain constant for a time equal to one-half of the free period. Under this force the pendulum will just swing out to the new position of equilibrium, where it is held on arrival by doubling the force. These cases have already been considered, but the analogue of the pendulum is instructive.

Kelvin* has shown that the equation of the second order

$$\frac{d}{dx}\left(\frac{1}{\mathrm{P}}\frac{dy_1}{dx}\right) = y_1 \tag{90}$$

can be solved by a machine. It is worth noting that an equation of the form (53) is solved at the same time. In fact, if we make

$$y_1 = \frac{dy_2}{dx}, \qquad \mathrm{P}y_2 = \frac{dy_1}{dx}, \tag{91}$$

we get on elimination either (90) for y_1, or

$$\frac{d^2y_2}{dx^2} = \mathrm{P}y_2 \tag{92}$$

for y_2. Equations (91) are those which express directly the action of the machine.

It now remains to consider more in detail some cases where total reflection occurs. When there is merely a simple transition from one medium (1) to another (2), the transmitted wave is

$$\phi_2 = \mathrm{A}_2 e^{-ia_2(x-x_1)}e^{i(ct+by)}. \tag{93}$$

If there is total reflection, a_2 becomes imaginary, say $-ia_2'$; the transmitted wave is then no longer a wave in the ordinary sense, but there remains some disturbance, not conveying energy, and rapidly diminishing as we recede from the surface of transition according to the factor $e^{-a_2'(x-x_1)}$. From (2)

$$a_2^2 = \frac{4\pi^2}{\lambda_2^2}\cos^2\theta_2 = \frac{4\pi^2}{\lambda_1^2}\left(\frac{\mathrm{V}_1^2}{\mathrm{V}_2^2} - \sin^2\theta_1\right),$$

or

$$a_2' = \frac{2\pi}{\lambda_1}\sqrt{(\sin^2\theta_1 - \mathrm{V}_1^2/\mathrm{V}_2^2)}. \tag{94}$$

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* 'Roy. Soc. Proc.,' 1876, vol. 24, p. 269.

It appears that soon after the critical angle is passed, the disturbance in the second medium extends sensibly to a distance of only a few wave-lengths.

The circumstances of total reflection at a sudden transition are thus very simple; but total reflection itself does not require a sudden transition, and takes place however gradual the passage may be from the first medium to the second, the only condition being that when the second is reached the angle of refraction becomes imaginary. From this point of view total reflection is more naturally regarded as a sort of refraction, reflection proper depending on some degree of abruptness of transition. Phenomena of this kind are familiar in Optics under the name of *mirage*.

In the province of acoustics the vagaries of fog-signals are naturally referred to irregular refraction and reflection in the atmosphere, due to temperature or wind differences; but the difficulty of verifying a suggested explanation on these lines is usually serious, owing to our ignorance of the state of affairs overhead.*

The penetration of vibrations into a medium where no regular waves can be propagated is a matter of considerable interest; but, so far as I am aware, there is no discussion of such a case, beyond that already sketched, relating to a sudden transition between two uniform media. It might have been supposed that oblique propagation through a variable medium would involve too many difficulties, but we have already had opportunity to see that, in reality, obliquity need not add appreciably to the complication of the problem.

To fix ideas, let us suppose that we are dealing with waves in a membrane uniformly stretched with tension T, and of superficial density ρ, which is a function of x only. The equation of vibration is ('Theory of Sound,' § 194)

$$\mathrm{T}\left(\frac{d^2\phi}{dx^2}+\frac{d^2\phi}{dy^2}\right)=\rho\frac{d^2\phi}{dt^2},$$

or, if ϕ be proportional to $e^{i(ct+by)}$, as in (1),

$$\frac{d^2\phi}{dx^2}+(c^2\rho/\mathrm{T}-b^2)\,\phi=0, \tag{95}$$

agreeing with (53) if

$$\kappa^2=c^2\rho/\mathrm{T}-b^2. \tag{96}$$

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* An observation during the exceptionally hot weather of last summer recalled my attention to this subject. A train passing at high speed at a distance of not more than 150 yards was almost inaudible. The wheels were in full view, but the situation was such that the line of vision passed for most of its length pretty close to the highly heated ground. It seemed clear that the sound rays which should have reached the observers were deflected upwards over their heads, which were left in a kind of shadow.

The waves originally move towards the less dense parts, and total reflection will ensue when a place is reached, at and after which κ^2 is negative. The case which best lends itself to analytical treatment is when ρ is a linear function of x. κ^2 is then also a linear function; and, by suitable choice of the origin and scale of x, (95) takes the form

$$\frac{d^2\phi}{dx^2}+\tfrac{1}{3}x\phi = 0. \tag{97}$$

The waves are now supposed to come from the positive side and are totally reflected at $x = 0$. The coefficient and sign of x are chosen so as to suit the formulæ about to be quoted.

The solution of (97), appropriate to the present problem, is exactly the integral investigated by Airy to express the intensity of light in the neighbourhood of a caustic.* The line $x = 0$ is, in fact, a caustic in the optical sense, being touched by all the *rays*. Airy's integral is

$$W = \int_0^\infty \cos \tfrac{1}{2}\pi (w^3 - mw)\, dw. \tag{98}$$

It was shown by Stokes† to satisfy (97), if

$$x \text{ (in his notation } n) = (\tfrac{1}{2}\pi)^{2/3} m. \tag{99}$$

Calculating by quadratures and from series proceeding by ascending powers of m, Airy tabulated W for values of m lying between $m = \pm 5{\cdot}6$. For larger numerical values of m another method is necessary, for which Stokes gave the necessary formulæ. Writing

$$\phi‡ = 2(\tfrac{1}{3}x)^{3/2} = \pi(\tfrac{1}{3}m)^{3/2}, \tag{100}$$

where the numerical values of m and x are supposed to be taken when these quantities are negative, he found when m is positive

$$W = 2^{\frac{1}{2}}(3m)^{-\frac{1}{4}}\{R\cos(\phi-\tfrac{1}{4}\pi)+S\sin(\phi-\tfrac{1}{4}\pi)\}, \tag{101}$$

where
$$R = 1-\frac{1.5.7.11}{1.2(72\phi)^2}+\frac{1.5.7.11.13.17.19.23}{1.2.3.4(72\phi)^4}-\ldots, \tag{102}$$

$$S = \frac{1.5}{1.72\phi}-\frac{1.5.7.11.13.17}{1.2.3(72\phi)^3}+\ldots. \tag{103}$$

When m is negative, so that W is the integral expressed by writing $-m$ for m in (98),

$$W = 2^{-\frac{1}{2}}(3m)^{-\frac{1}{4}}\epsilon^{-\phi}\left\{1-\frac{1.5}{1.72\phi}+\frac{1.5.7.11}{1.2(72\phi)^3}-\ldots\right\}. \tag{104}$$

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* 'Camb. Phil. Trans.,' 1838, vol. 6, p. 379; 1849, vol. 8, p. 595.

† 'Camb. Phil. Trans.,' 1850, vol. 9; 'Math. and Phys. Papers,' vol. 2, p. 328.

‡ Here used in another sense.

The first form (101) is evidently fluctuating. The roots of $W=0$ are given by

$$\phi/\pi = i - 0{\cdot}25 + \frac{0{\cdot}028145}{4i-1} - \frac{0{\cdot}026510}{(4i-1)^3} + \ldots, \tag{105}$$

i being a positive integer, so that for $i = 2, 3, 4$, etc., we get

$$m = 4{\cdot}3631,\ 5{\cdot}8922,\ 7{\cdot}2436,\ 8{\cdot}4788, \text{ etc.}$$

For $i = 1$, Airy's calculation gave $m = 2{\cdot}4955$.

The complete solution of (97) in series of ascending powers of x is to be obtained in the usual way, and the arbitrary constants are readily determined by comparison with (98). Lommel* showed that these series are expressible by means of the Bessel's functions $J_{\frac{1}{3}}$, $J_{-\frac{1}{3}}$. The connection between the complete solutions of (97), as expressed by ascending or by descending semi-convergent series, is investigated in a second memoir by Stokes.† A reproduction of the most important part of Airy's table will be found in Mascart's 'Optics' (vol. 1, p. 397).

As total reflection requires, the waves in our problem are stationary as regards x. The realised solution of (95) may be written

$$\phi = W \cos(ct + by), \tag{106}$$

W being the function of x already discussed. On the negative side, when x numerically exceeds a moderate value, the disturbance becomes insensible.

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* 'Studien über die Bessel'schen Functionen,' Leipzig, 1868.

† 'Camb. Phil. Trans.,' 1857, vol. 10, p. 106.

The Testing of Plane Surfaces.

By P. E. Shaw, B.A., D.Sc.

(Communicated by Prof. J. H. Poynting, F.R.S. Received December 9, 1911—Read January 25, 1912.)

There is only one way of originating a true plane, viz., to make it in triplicate and to work all three surfaces so as to obtain a "fit" between them. In engineering trade practice this is done when a standard plate is required, and any one of the three plates thus obtained can be used as being truly plane (within the limits of the "raddle" process) for the making of further surface-plates.

In many modern exact apparatus, *e.g.*, a standard measuring machine or a Michelson's interferometer, accuracy of measurement directly depends on the truth of the plane "ways" of the bed along which the various parts of the apparatus slide. These ways are made either by scraping or lapping, and it is of importance to know what errors occur from place to place along the bed due to defective workmanship. The bed generally has three worked planes all inclined to one another, and the movable parts rest on these by five contact points, thus allowing only one degree of freedom. These five feet bear on the surfaces below by small areas, and amongst other considerations it is important to know how far these feet rise and fall in and out of the scraping marks if the surfaces have been made by scraping.

Any such rise and fall produces a rocking motion in a movable part as it slides along the bed. In a badly made surface such pits would be wide and deep and the attendant rocking motion considerable. But any surface, whether scraped or lapped, is liable to have constant or variable curvature over a large area due to defective workmanship or due to warping subsequent to manufacture.

It is convenient for present purposes to denote the small local irregularities as *ripples* (only found on scraped surfaces) and the large changes in curvature as *waves*. Any tool used to test for ripples must have small feet, whereas for waves one would need an appliance with feet of such large area as would not fall into scrape marks.

The object of this paper is to indicate ways of measuring these errors in surface-plates. The writer recently had a measuring machine made. Its purpose was to apply to end-standards of length very severe tests as to length and figure; and for this purpose one must be sure that errors of the first order, due to inequalities in the bed, will not enter the results. In the *making of the bed more than usual care was taken in casting the bed and in* "ageing" it with repeated planing and finally with various stages of scraping.

The principal headstock of the machine has a long base (18 inches). Suppose this headstock is placed on the bed and a sensitive spirit level mounted on it; if it be moved along the bed, then, supposing the three cardinal planes of the bed are true planes, it will move along without rocking and the spirit level will remain at rest. But any error, whether ripple or wave, in the bed would be shown by the level. Very sensitive spirit levels can be made, but exact quantitative results are required, and it would not be easy to calibrate such a device, besides which, if it is sensitive, it must have a very limited range. Moreover it could only be used for a level surface and would not be generally applicable to testing plane surfaces which are often inclined *in situ* to the horizon. So a spirit level device will not serve our purpose.

Again a spherometer will not do, as we have to test a surface which has considerable length but small breadth. In short, there is no apparatus or method in use suitable for the purpose, so one must be invented.

Surface-tester No. 1.—The first device adopted is shown in fig. 1. A stout bar, 20 inches long, of teak is fitted with (1) a micrometer screw in the centre and with (2) two feet, half an inch apart, set in a line across the bar at one end, and (3) one foot at the other end of the bar.

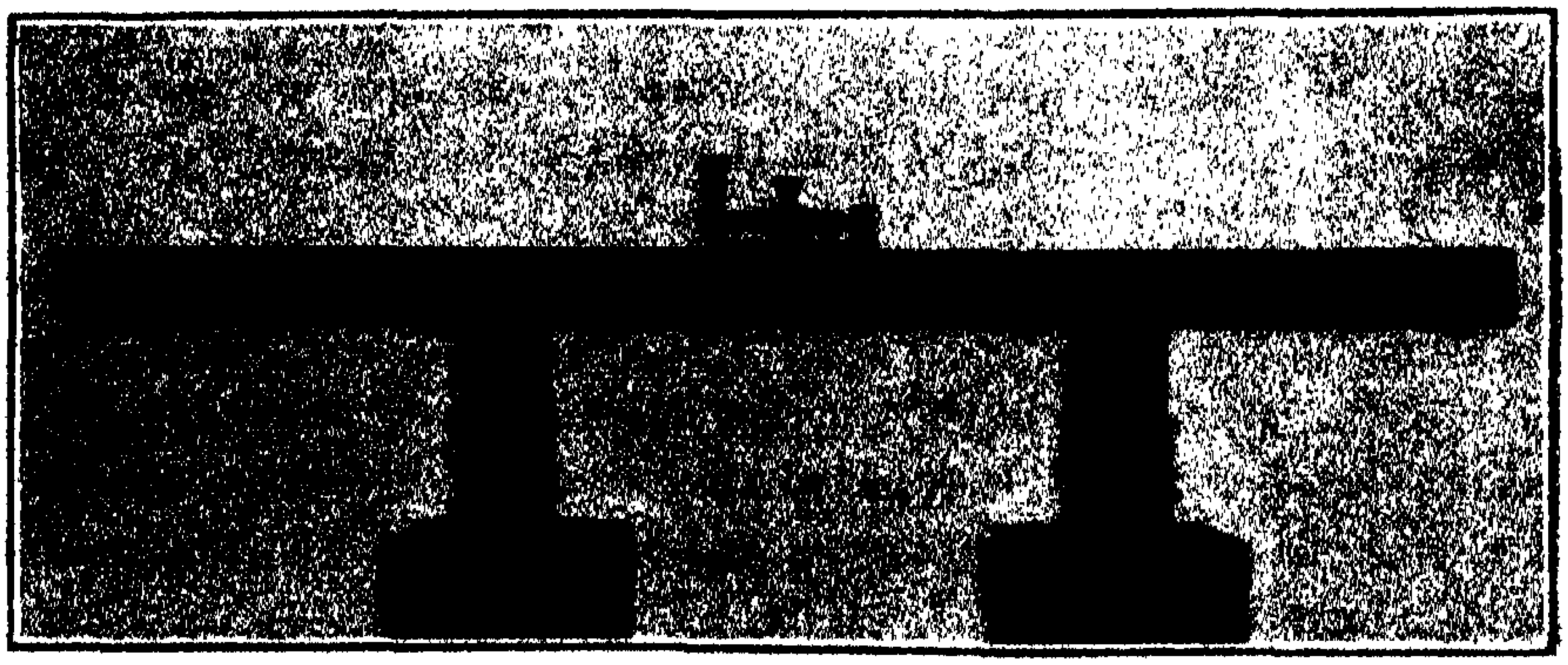

Fig. 1.

All the feet are studs just flattened, such as would be found on a rounded foot which has been worked to and fro several times on a flat surface. The micrometer screw being "in," the apparatus, which is akin to a spherometer, would rest stably on a surface plate. There is a binding screw attached to the micrometer. A circuit of a simple cell, resistance box, and telephone receiver is joined to the binding screw and the surface-plate. By working the micrometer "out" electric contact is made when the screw point reaches the surface-plate, and the micrometer is read when the telephone sounds.

Calling the three cardinal surfaces of the bed *a*, *b*, *c*, the following measurements were taken at equal intervals along the length of the bed. The units are 1/10000 inch.

	a.	*b*.	*c*.
	144	143	144
	144	146	142
	143	144	142
	142	144	144
	144	145	144
	144	144	144
	140	144	144
Means	143	144·3	143·5
		Mean of means......	143·6

These surfaces agree, therefore, throughout, to 4/10000 inch for measured lengths of about 16 inches. The rounded mean reading is 143·6. But we have no method, with surface-tester No. 1, of finding the true zero reading. The above surfaces may be all convex or all concave, or the mean reading may be nearly true zero.

The surface-tester was then tried on a new, well-made, scraped surface-plate, the readings being

140 142 140 139 141 142 142 140 140 Mean...... 140·7

If we could assume this plate to be very good, we might take the reading 140·7 to be true zero (*i.e.* the reading which a geometrical plane surface would give), in which case the mean error of the surfaces *a*, *b*, *c*. would be 3/10000 inch in a length of 16 inches. But it is not permissible to assume the truth of any "standard," so the following modification of the above apparatus was made to determine true zero reading.

Surface-tester No. 2.—A stout bar of iron (fig. 2) with a deep vertical web

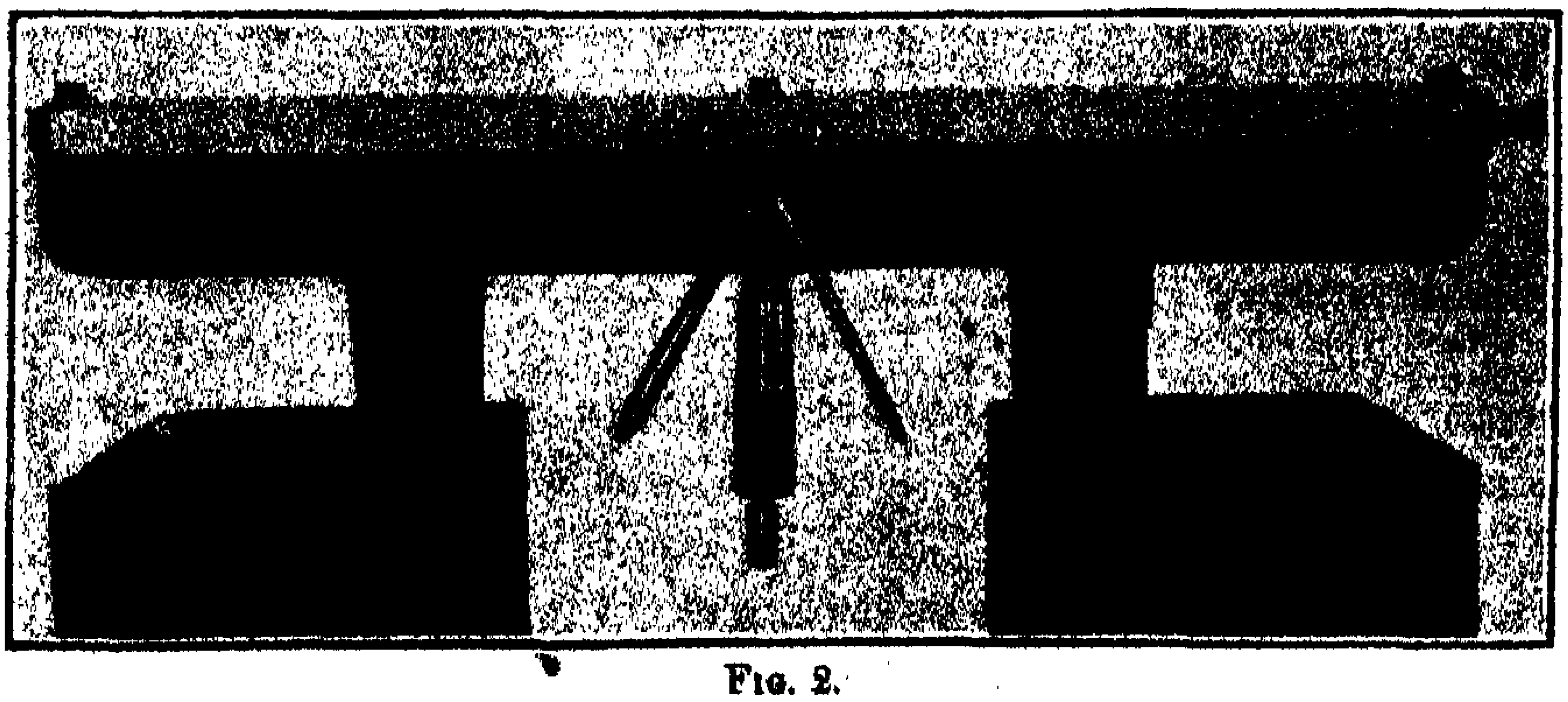

Fig. 2.

has let into its lower face two hardened steel studs with true flat feet of ¼ inch diameter. These studs are 12 inches apart. Midway between them is fixed in the bar a Brown and Sharp micrometer screw, whose working end is another true flat surface ¼ inch diameter. The studs are bushed, and a binding-screw is let into the bar to enable a circuit to be made just as in tester No. 1. Great care must be taken, when using the testers, that no shocks are received by micrometer and studs. Guards are shown, one on each side of the micrometer. Also, when not in use, the testers are packed away carefully.

This instrument is made in duplicate. Call the two testers A and B. Place A on the surface to be tested. If the micrometer screw is "in," A would rest stably on a flat surface, the end feet touching the latter at places, say *d* and *e*. On screwing in the micrometer, contact is made when the latter reaches the surface. Lift the tester from the surface and place it, feet upwards, on a suitable cradle (see fig. 2). Next take the tester B and place it on the surface, its feet resting on places *d* and *e*; adjust the micrometer to contact. Take a reading of B; call it B_1. Place B on A as shown in fig. 3.

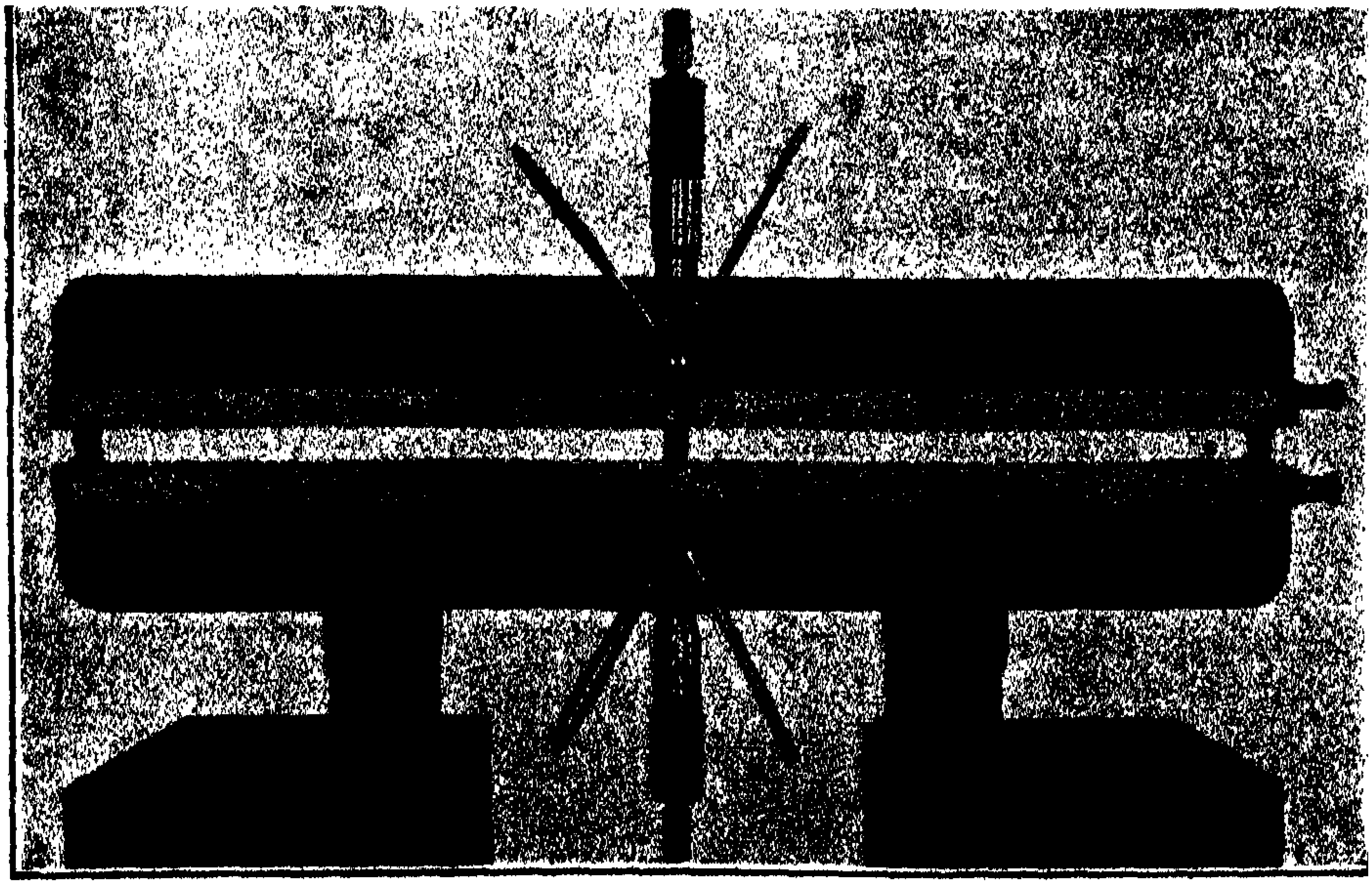

Fig. 3.

If the centre feet of A and B just meet in the above position, B_1 is true zero reading and the surface is a true plane, at least as regards places *d*, *e*, and the place on the surface midway between them. If, on the other hand, the micrometer of B has to be screwed in or out to just meet the screw of A, giving reading B_2, we have $\frac{1}{2}(B_1-B_2)$ as the error of the three places from a straight line. Screwing in shows convexity, and screwing out concavity of the surface. True zero reading is $B_1 + \frac{1}{2}(B_1 - B_2)$.

The process used is akin to the three-surface method mentioned at the beginning of the paper.

A small flexure of the tester occurs, due to its own weight. To avoid this, the supporting blocks under A in the cradle are placed at the Airy points along the bar as shown. Before B rests on A, this arrangement would leave A slightly concave upwards, but when B is placed on A this concavity would be reduced to zero by the weight of B.

For tester No. 2 mechanical contact is simplest, but for tester No. 1 electric contact is more accurate.

In order to obtain true zero reading, we have had to resort to micrometry with flat faces (tester No. 1 would obviously not serve). One great disadvantage of employing flat faces in micrometry is that the errors in truth of these faces enter into the results directly. Surface-tester No. 2 will be of small service unless the highest possible mechanical skill is put into the setting of its three feet in one plane for true zero.

Mr. A. Jenkinson, of the National Physical Laboratory, Teddington, an experienced micrometer maker, undertook to make the two testers No. 2 to meet my requirements, and his work proved very satisfactory. He proceeded as follows :—

Castings were made and were machined and bored roughly to remove casting strains. They were then left for a period in a vibrational place to settle. Machining was repeated. The bottom was scraped true, then clamped to a lathe face-plate and the hole for the micrometer bored out. The holes for the other two feet were reamered to size through a true jig plate. The studs were turned and hardened and were settled in boiling water; they were then pressed into place with bushes. The micrometer was then put into its place and the two other feet lapped by hand till they were true with the micrometer foot. This last process took considerable time and trouble, as on it hangs the accuracy of results.

As examples of the use of the surface-testers the following cases are given :—

I. Hexagon Surface-Plate (2 feet diameter).—Using tester No. 2, nine positions were taken symmetrically round the centre of the plate. In some cases repetition was made to ascertain whether any change due to temperature occurred as the measurements proceeded.

Position.	Reading B_1.	Reading B_2.	Zero reading $B_1 + \frac{1}{2}(B_1 - B_2)$.	Error $\frac{1}{2}(B_1 - B_2)$.
1	17	14	15·5	1·5
2	17	13·5	15·3	1·8
3	17	14	15·5	1·5
4	18	13·5	15·7	2·2
5	18	14	16	2
6	18	13·5	15·7	2·2
7	18·5	14	16·2	2·2
8	17·5	13·5	15·5	2
9	17·5	13·5	15·5	2
7	18	14	16	2
1	17	14	15·5	1·5
			Mean... 15·7	Mean... 1·9 (convex)

As before the unit is 1/10000 inch.

This plate is consistently convex at regions about the centre, the error on a length of 12 inches being on the average about 1/5000 inch.

A set of readings like the above establishes an accurate true zero reading (15·7 in this case). The divergence from this value is at most 0·4/10000 in the table above. This irregularity may be due to defects in the testers or to the impossibility of placing both testers on the same places exactly, or to both causes.

Having discovered true zero for B we need not use A further, for the reading B, together with true zero, gives the error of the surface.

A set of readings taken round the edge of the above surface plate gives us results as below :—

B_1........................	17·5	18	17	16	16·5	16	17	18	16	16
Error, $B_1 - 15·7$...	1·8	2·3	1·3	0·3	0·8	0·3	1·3	2·3	0·3	0·3 (convex)

Thus the mean error near the edge of the plate is less than near its centre, but the plate is more irregular.

Having ascertained the general contour of the surface by tester No. 2 we look for ripples near the centre of the plate by tester No. 1 and obtain readings :—

172 172 172 171·6 171·6 171·6 171·6 172 172·4 Mean...... 171·9

The units are again 1/10000 inch. The extreme readings here differ from the mean reading by about the same amount as when the tester No. 2 was used. So the ripples are a negligible quantity in this plate. In some plates, however, one finds ripples in evidence.

II. Two small surface-plates (10 inches by 8 inches), one lapped and one scraped, were very carefully made, and were tested soon after manufacture. As is seen below they are so good that errors of observation by the micrometer are of the same order as errors of the surface. Probably at present surface-plates are not required and cannot be made as a commercial proposition to higher accuracy. But if such should ever be the case the surface-testers would have to be made more sensitive. This could be done by having a larger divided drum on the micrometer and by using electric contact.

Ten places are chosen and readings repeated at each for each of the above surfaces. True zero for tester A is 56 and for B is 62·7. For the lapped surface both A and B were employed; for the scraped surface A only, further trial being unnecessary. Results:—

Position.	Lapped plate.				Scraped plate.	
	Tester A.		Tester B.		Tester A.	
1	56	56	62	62·5	56·5	57
2	56	55·5	62	62·5	56·5	56
3	56·5	56	62·5	62·5	56	56
4	56	56	62·5	63	56·5	56
5	56	56	62	63	56	56
6	56	55·5	62	62·5	56	56
7	56	55·5	62	62·5	57	56
8	55·5	56	62	62·5	56	55·5
9	55·5	55·5	62·5	63	56	56·5
10	55·5	55·5	62·5	62·5	56·5	56·5
	Mean error ...... 0·1		Mean error ...... 0·3		Mean error ...... 0·2	

The readings on any surface differ by 1/10000 inch only, and the mean errors are only 1/100000 inch, 3/100000 inch, and 2/100000 inch.

The mean error in the lapped plate is a convexity and in the scraped plate a concavity.

The above plates are too small for observation by tester No. 1.

III. Experiments on Plate Glass.—Of all cheap commercial articles this has plane faces with the nearest approach to truth. As regards small areas the two surfaces are so nearly plane that reflection and refraction at them appears, by ordinary tests, to be regular. It is of interest to discover how nearly the surfaces taken on large areas approach truth.

Surface-tester No. 2 is used. Four specimens, taken from the stock of one of the largest manufacturers of plate glass, gave results shown in the following table. A length of plate was placed on two narrow wooden strips so that when the tester rested on the glass its feet would lie vertically over the strips. The strips would take up the weight of the tester and prevent flexure of the plate.

		Reading A_1.	Reading A_2.	Zero.	Mean plate error.
I	Front	289 242	296 294	267·5 268 } Mean 267·7	27·2 concave
	Back	300 298			31 convex
II	Front	273 272			4·5 convex
	Back	253 253			15 concave
III	Front	295 294			26·5 convex
	Back	249 246			20·5 concave
IV	Front	272 271			3·5 convex
	Back	263 264			4·5 concave

Thus the errors vary from 30/10000 to 3/10000 for these specimens. The fourth specimen has an accuracy which compares well with that of a surface-plate. When once the zero reading (267·7 here) has been found, it is an easy matter to test the plates quickly and pick out a good one.

In all cases the plates are curved as a whole, one side being convex, the other concave.

I am glad to acknowledge that the cost of the apparatus was defrayed by a Government grant from the Royal Society.

Note on the Scattering of α-Particles.

By Dr. H. Geiger, Lecturer in Physics, Manchester University.

(Communicated by Prof. E. Rutherford, F.R.S. Received December 13, 1911,—
Read January 25, 1912.)

In a previous paper on the scattering of the α-particles by matter the author has described experiments which allowed a direct determination of the most probable angle through which an α-particle is deflected when passing through a thin film of matter.* In these experiments an intense, narrow and parallel pencil of α-particles was allowed to fall on a zinc sulphide screen, and the distribution of the scintillations over that screen was determined when the pencil was intercepted by sheets of metal of various thickness and material. Measurements were also made for α-particles of varying speed. From this distribution the most probable deflection suffered by the α-particle in each particular case was easily deduced. These deductions were based on the assumption that the scattering of the pencil is the result of a multitude of small deflections suffered by the α-particles in their encounters with the atoms of the scattering foil. This type of scattering has recently been termed by Rutherford† "compound scattering" in order to distinguish it from another type, denoted as "single scattering," which concerns the deflections through large angles of an α-particle in a single collision.

The first section of this paper deals with the distribution of the scattered α-particles on the screen; the second discusses the connection between the thickness of foils and the most probable angle of scattering which they produce. It will not be necessary to make any special assumptions as to the laws of action and reaction between the atom and the α-particle; it suffices only to suppose that the deflection in each single collision is small compared with the final deflection after passing through the scattering foil. This paper, therefore, does not deal with the large scattering observed by Geiger and Marsden‡ which has been ascribed by Rutherford to single collisions. Such large deflections are rare, and can be neglected in the consideration of the deflections through small angles.

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* H. Geiger, 'Roy. Soc. Proc.,' 1910, vol. 83, p. 492.

† E. Rutherford, 'Phil. Mag.,' 1911, vol. 21, p. 669.

‡ H. Geiger and E. Marsden, 'Roy. Soc. Proc.,' 1909, vol. 82, p. 495.

(1) *Distribution Curve of the α-Particles.*

A parallel pencil of α-particles of infinitely small cross-section is supposed to pass through a scattering foil and then to fall upon a zinc sulphide screen. Taking rectangular co-ordinates in the plane of the screen with the point of incidence of the unscattered beam as origin of the system, the angle through which an α-particle is turned when passing through the foil may be measured by the co-ordinates of the point of impact of this particle on the screen. This is justifiable, since all scattering takes place at the same distance from the screen, and since we are only dealing with very small angles of the order of a few degrees. By the law of errors we find that the probability of p of an α-particle hitting the element $dx\,dy$ at the point x, y of the screen is given by

$$p = \frac{1}{2l^2\pi} e^{-(x^2+y^2)/2l^2} dx\,dy. \tag{1}$$

Introducing polar co-ordinates and integrating with respect to the angle between 0 and 2π we obtain the probability P_r of any deflection r from the centre, namely,

$$P_r = \frac{r}{l^2} e^{-r^2/2l^2} dr. \tag{2}$$

The curve represented by this equation has a maximum for $r = l$, and l is therefore the most probable deflection on the screen, or l/d is the most probable angle of deviation, d being the distance from scattering foil to screen.

The average value of r is found by integrating rP_r from 0 to ∞. The result is $\bar{r} = \frac{1}{2} l \sqrt{(2\pi)}$ or 1·25 l approximately. The average deflection is therefore 1·25 times greater than the most probable deflection.

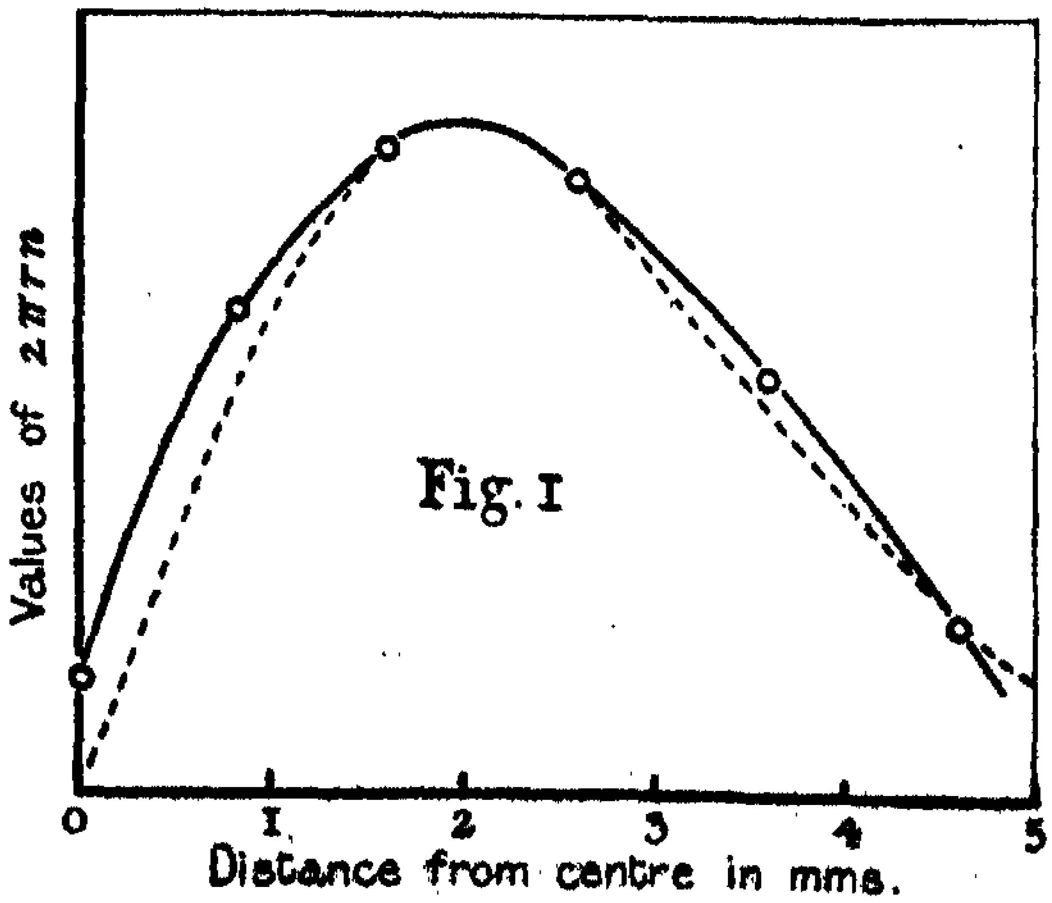

Fig. I

The curve represented by the above equation is in good agreement with the experimental curves which were given in figs. 2 and 3 of the paper quoted above. For comparison, the curve of fig. 2 is drawn again in the accompanying diagram (fig. 1 of this paper), the theoretical curve being represented by the dotted line. The most probable deflection l is taken equal to 2. The difference between the two curves near the origin is due to the finite cross-section of the beam used in the experiment.

(2) *Variation of Scattering Angle with Thickness of Foil.*

We must first discuss the composition of successive scattering angles. Let us assume that a scattering foil F placed at a distance d from the screen may scatter the α-particles so that a most probable deflection l_1 is obtained on the screen. The probability p_1 that an α-particle hits an element $dx_1\,dy_1$ at the point x_1, y_1 of the screen is then given by

$$p_1 = \frac{1}{2\pi l_1^2} e^{-(x_1^2+y_1^2)/2l_1^2} dx_1\,dy_1. \tag{3}$$

Let us next consider the effect of an additional scattering foil placed directly in front of the first one. Let the second foil *alone* produce a most probable deflection l_2 of an α-particle on the screen. *Combined* with the first foil it will produce an additional deflection of the particle from the point x_1, y_1 to the point x_2, y_2. The probability p_2 of this deflection is

$$p_2 = \frac{1}{2\pi l_2^2} e^{-[(x_2-x_1)^2+(y_2-y_1)^2]/2l_2^2} dx_2\,dy_2. \tag{4}$$

The probability that the α-particle, after passing through the two foils, hits the screen at the point x_2, y_2 is given by the integral with respect to x_1, y_1 of the product of the two independent probabilities p_1 and p_2.

This probability is :—

$$\mathrm{P} = \frac{dx_2\,dy_2}{4\pi^2 l_1^2 l_2^2} \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} e^{-[l_2^2(x_2^2+y_2^2)+l_1^2(x_1-x_2)^2+l_1^2(y_1-y_2)^2]/2l_1^2l_2^2} dx_1 dy_1.$$

The exponent may be written in the form

$$-\frac{x_2^2+y_2^2}{2(l_1^2+l_2^2)} - \frac{1}{2l_1^2l_2^2(l_1^2+l_2^2)}[\{x_1(l_1^2+l_2^2)-x_2l_1^2\}^2+\{y_1(l_1^2+l_2^2)-y_2l_1^2\}^2],$$

and the integration can now be carried out independently for x and y between the limits $-\infty$ and $+\infty$. We obtain

$$\mathrm{P} = \frac{1}{2\pi(l_1^2+l_2^2)} e^{-(x_2^2+y_2^2)/2(l_1^2+l_2^2)} dx_2\,dy_2. \tag{5}$$

Again introducing polar co-ordinates and integrating with respect to the angle, we obtain the probability of a deflection of magnitude r on the screen independent of the direction of this deflection,

$$P = \frac{r}{l_1^2 + l_2^2} e^{-r^2/2(l_1^2+l_2^2)} dr. \tag{6}$$

This equation is identical with equation (2) except that in this case the constant $l_1^2 + l_2^2$ appears in place of l^2. Consequently, if l_1 and l_2 denote the most probable deflections produced by the foils 1 and 2 independently, then the most probable deflection produced by foils 1 and 2 combined is $\sqrt{(l_1^2 + l_2^2)}$. The above analysis can be extended from two to three foils, and so on. In the case of n foils the most probable deflection is $\sqrt{(l_1^2+l_2^2+l_3^2+\ldots+l_n^2)}$, where $l_1, l_2, \ldots, l_n$, are the most probable angles of deflections produced by each foil separately.

If we consider foils of equal thicknesses and assume that the velocity of the particle does not change in passing through them, we can put $l_1 = l_2 = l_3 = l_n$. Thus it follows that the most probable angle of scattering increases as the square root of the thickness traversed by the particle. This has also been pointed out by Sir J. J. Thomson in a theoretical paper in the 'Proceedings of the Cambridge Philosophical Society,' 1910.

We will now modify the equation obtained above for the variation of the scattering angle with thickness by taking account of the decrease of the velocity of the α-particle when it passes through the foil. On account of the decrease of the velocity the specific scattering coefficient increases, and, as has been shown by experiment with very thin foils, the increase is inversely proportional to the third power of the velocity. In order to deduce the scattering produced by a foil of finite thickness we shall, for convenience, consider that foil as being made up of a number of foils of such thickness that the α-particle in passing through one of them collides with one atom only. If n_0 denotes the range of an α-particle expressed as the number of atoms through which it can penetrate, then its velocity after it has passed through n atoms is given by

$$v^3 = \frac{v_0^3}{n_0}(n_0 - n),$$

and the most probable deflection produced by the nth atom will be

$$l = l_0 \frac{v_0^3}{v^3} = l_0 \frac{n_0}{n_0 - n},$$

where l_0 is the most probable deflection for $v = v_0$, v_0 being the initial velocity of the α-particle.

When the α-particle passes through the first atom, the value of the most probable deflection is $l_1 = l_0 \frac{n_0}{n_0 - 1}$, when it passes through the second the value of l is $l_2 = l_0 \dfrac{n_0}{n_0-2}$, and so on. The square of the most probable deflection of the particle, after it has passed through n atoms in succession, is given by

$$L^2 = l_1^2+l_2^2+l_3^2+\ldots+l_n^2 = n_0^2 l_0^2\left[\frac{1}{(n_0-1)^2}+\frac{1}{(n_0-2)^2}+\ldots+\frac{1}{(n_0-n)^2}\right],$$

or, since n is large,

$$L^2 = n_0^2 l_0^2 \int_0^n \frac{1}{(n_0-x)^2}\,dx, \text{ leading to } L = l_0\sqrt{\frac{n_0 n}{n_0-n}}.$$

The curve represented by this equation is drawn in fig. 2. According to this relation, the most probable angle of scattering increases for small thicknesses (n small compared with n_0), according to the square root of the thickness. With further increase of thickness, the curve passes through a point of inflection, and is, in fact, nearly a straight line over an appreciable range. For still larger thicknesses, the increase of the most probable angle becomes more and more rapid.

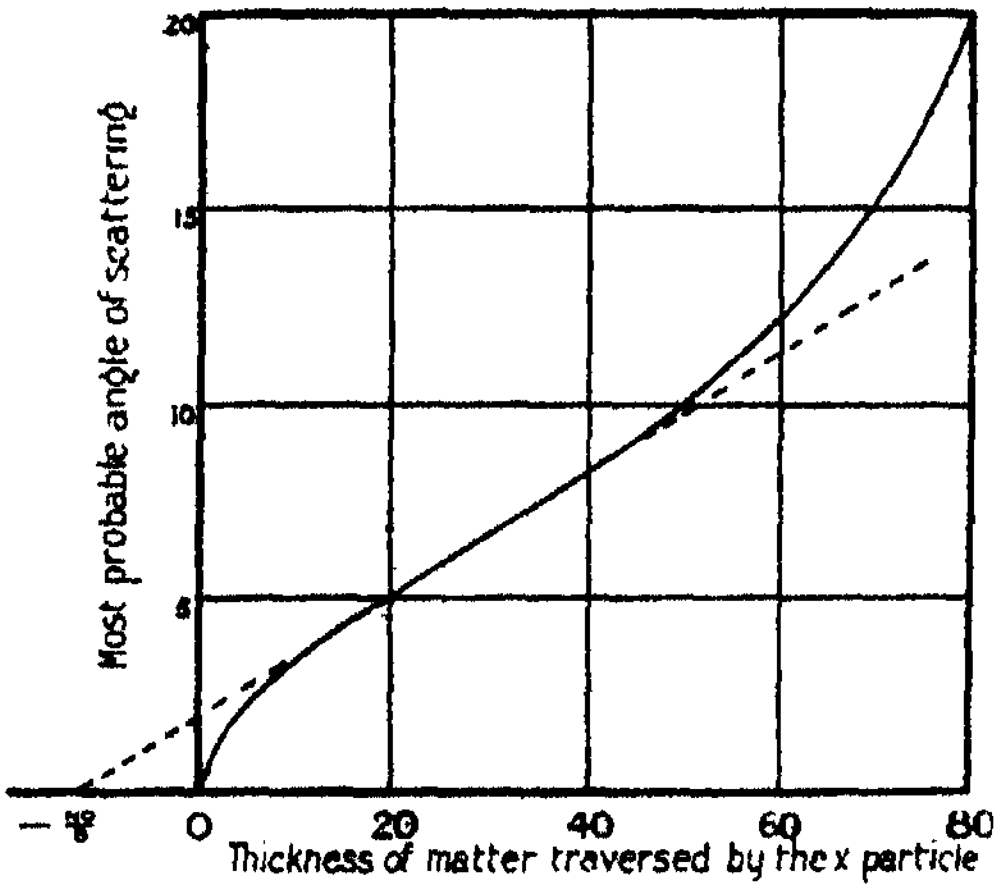

FIG. 2.

The experimental curves, which were given in fig. 5 of the previous paper, are in good agreement with these deductions. Starting from the origin, the experimental curves obtained for different materials show a distinct curvature before they turn into straight lines. The experiments were not carried out with sufficiently large thicknesses to show the final rapid increase of the scattering angle. The range of thickness over which the scattering was investigated corresponds to abscissæ in the above figure smaller than 60. The straight lines obtained in the experiments mentioned above, if produced backwards, all cut the negative X axis at nearly the same distance from the origin. This is also in agreement with the equation, since the tangent at the point of inflection cuts the X axis at the point $-\frac{1}{8}n_0$, a quantity which is independent of the specific properties of the scattering material.

From similar considerations to those given above, it is possible to calculate the scattering of α-particles in gases, and to deduce the scattering coefficients. This question is of interest, since for substances of atomic weight comparable with that of the α-particle, the amount of scattering may not be proportional to the atomic weight, a relation which seems to hold fairly well for the heavier atoms so far examined. A discussion of this will, however, be postponed until the necessary experiments have been carried out.

I take this opportunity of expressing my thanks to Prof. Rutherford for many helpful suggestions.

The Effect of Temperature upon Radioactive Disintegration.

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1. *Introduction.*

Within the last few years the influence of high temperature on the activity of radium emanation, of the active deposit, and of radium C has been examined in detail by several authors. The conclusions arrived at have been conflicting, some workers affirming a positive effect of temperature, others denying it. This lack of agreement is due, however, to a difference in the method of measurement of the active matter under investigation. Those workers who measured the activity by γ-rays are all agreed that temperature has no effect whatever, while those who measured by β-rays found always an effect of some kind, in many cases of considerable magnitude, and often, indeed, of a very surprising nature.

While, however, the fact that there is a β-ray effect is admitted by all, there is still a lack of agreement between the results of the experiments of different workers, and even of different experiments of the same worker, which is hardly to be expected if the effects were due to a definite change in the properties of the disintegrating atoms at high temperatures. In view, therefore, of the uncertainty which has arisen on a point of such great theoretical importance, a systematic investigation was necessary to obtain definite results, whether positive or negative. This the author, at the request of Prof. Rutherford, has carried out.

Work on β-Rays.—The original experiments of Curie and Danne[*] showed that the rate of decay of radium C could be altered by subjecting it to temperatures above 630°. Bronson, however, found[†] that the more volatile radium B had a longer period of change than radium C, instead of the contrary as previously supposed, and showed that, when this fact is taken into consideration, the anomalies in question are capable of a complete explanation.

Makower,[‡] working with radium emanation inside tubes of sealed quartz, found, however, that the β-radiation from radium C was reduced in intensity from 4 to 15 per cent. by heating the tube to temperatures over 1000°, the measurements being conducted in the cold. The effect was temporary only, the normal activity of the tube being reached again after it had been left for an hour at room temperature.

In later experiments with Russ[§] the same author found that, while the β-activity of the emanation was distinctly lower at high temperatures than at room temperature, it decayed at 1100° at the normal rate. The β-activity of the active deposit on a wire inside a sealed quartz tube showed also a somewhat irregular diminution of from 3 to 15 per cent. for temperatures between 900° and 1500°. As a result, measurement of the decay of the active deposit, with the tube at first cold, and subsequently subjected to a high temperature, showed an apparent increase in the rate of decay, and *vice versâ*.

Engler,[||] working on the same lines as Makower and Russ, measured the β-activity both of the emanation and of the active deposit during heating and cooling, as well as when a steady temperature had been reached. With the emanation itself in the quartz tube, a rapid increase in the activity was always observed on heating. Cooling brought the activity at first below the room temperature value, but after an hour in the cold the activity regained its original value. In some experiments, cooling did not cause a decrease of the activity below the normal value at all. Heating the active deposit to 1100° or 1200° caused a decay more rapid than the normal, which gradually became normal as the heating was maintained. On cooling, the decay was at first less than, but later increased to, the normal.

[*] 'Compt. Rend.,' 1904, vol. 138, pp. 748—751.

[†] 'Phil. Mag.,' 1906, vol. 11, p. 810.

[‡] 'Roy. Soc. Proc.,' 1906, A, vol. 77, p. 241.

[§] 'Roy. Soc. Proc.,' 1907, A, vol. 79, p. 158.

[||] 'Ann. Physik,' 1908, vol. 26, p. 518.

Schmidt and Cermack,* using radium itself as a source of β-ray activity, showed that, while there is no permanent effect of high temperature on the β-radiation, the rays show a somewhat complex sequence of variations of activity, which is explained as being due to changes in their absorption by the preparation itself. (*a*) The first effect of heating to 1000° is to liberate the occluded emanation and to volatilise the products radium A, B, and C from the preparation, causing a lessened absorption and consequent sudden increase of β-radiation. (*b*) On cooling, the products, all except the emanation, are suddenly absorbed again by the preparation, with a consequent sudden return of the β-radiation to its initial value. (*c*) Three hours afterwards a new set of products is produced on the walls of the containing tube from the liberated emanation, which causes the β-radiation gradually to return to the higher value. (*d*) Then over a period of three weeks the liberated emanation decays, while fresh emanation is produced within the solid preparation, producing a gradual decay of the β-rays to their initial value.

The explanation (*b*) seems, however, very unlikely, and it will be shown later that the effect described in (*b*) and part of the effect described in (*a*) may be obtained in a sealed tube in which no solid matter whatever is present.

Work on γ-Rays.—The experiments of Bronson† on the γ-rays from a source of radium, of Engler‡ and of Schmidt§ on the γ-rays from radium emanation, from the active deposit and from radium C itself, show conclusively that there is no detectable effect of high temperatures on the intensity or nature of γ-rays. Rutherford and Petavel‖ showed also that the γ-radiation from radium emanation exposed momentarily to a pressure of about 1200 atmospheres and a temperature not lower than 2500°, produced by an explosion of cordite, was not altered at the moment of explosion. A 9 per cent. temporary reduction of the activity found after the explosion was due to a change of distribution of radium C inside the bomb, caused by its volatilisation and subsequent condensation, and was of the amount to be expected theoretically.

It is seen that the point at issue concerns itself entirely with the β-rays. The one abnormality, upon which all experimenters are agreed, is that a temporary increase or decrease of activity takes place at high temperatures, the departures from the normal activity disappearing entirely after the source has been kept at room temperature for three hours. The results of this paper show that this effect is due to a change of distribution of the active matter in the tube. The conclusion is reached that neither the β- nor the γ-ray activities of radium C, of the active deposit, or of the emanation, suffer any change, either in amount of activity or in rate of decay, at high temperatures. The author has succeeded in obtaining all of the abnormal effects of the workers whose experiments he has repeated. They can be completely explained by taking into consideration the change in average path of the β-rays through the quartz tube containing the active source caused by :—

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* 'Phys. Zeit.,' 1910, vol. 11, p. 793.

† 'Roy. Soc. Proc.,' 1907, A, vol. 78, p. 494.

‡ *Loc. cit.*

§ 'Phys. Zeit.,' 1908, vol. 9, p. 113.

‖ 'Brit. Assoc. Report,' 1907, Section A, p. 456.

(1) Changes of distribution of radium C inside the tube, arising from the volatilisation of radium C and radium B from the hotter to the cooler part, at all temperatures greater than 300°, and especially from 650° upwards.

(2) A change with temperature in the partition of radium C between the walls of the quartz tube and the volume enclosed.

2. *Experimental Disposition.*

The electroscope used was of lead, 7·5 cm. cube, and of 0·3 cm. wall thickness. One side, through which the rays passed, was of aluminium, 0·01 cm. thick. For γ-ray measurements a thick plate of lead (1·8 cm.) or of iron (0·6 cm.) was placed against this aluminium window.

The furnace consisted of a silica tube 12·5 cm. long, 2·2 cm. inside diameter, open at both ends, round which was wound a platinum wire, the whole being jacketed with kieselguhr for thermal insulation. Temperatures were measured with a Pt—Pt-Rh thermo-couple. Measurements were not carried usually beyond 1150° C., which was reached without any difficulty. The active material under investigation was in tubes of sealed quartz and mounted centrally in the furnace by means of thin nickel wire. When thus mounted, there was an unintercepted path between every point of the tube and the electroscope. Their distance apart was 40 to 60 cm.

3. *Experiments on Radium C.*

Pure radium C was deposited on nickel by v. Lerch's method, and the nickel sealed in a thin quartz tube. The decay of the radiations over a period of three hours was measured, the tube being kept at a temperature of 1150° for the first 90 minutes, and at room temperatures for the second. The β-rays were measured over the whole period, the γ-rays only at the high temperatures. The radiations, whether β or γ, at high temperatures and low temperatures alike, decayed exponentially, falling to half value in about 19·4 minutes.

In a second experiment the decay of the β-rays was measured for 65 minutes at a temperature of 1220°, but no difference in the value of the half-value period was obtained. Neither the β- nor the γ-rays of radium C are thus affected by high temperatures.

4. *Experiments on the Active Deposit.*

Purified emanation was forced into a little quartz bulb 0·3 cm. outside diameter, 0·25 mm. wall thickness, left there four hours, and then pumped out and the bulb sealed off. Measurements of γ-rays were started after 20 minutes, and continued at intervals for three hours. Measurements of β-rays were started after 85 minutes, and continued for five hours after sealing off.

All the γ-ray observations lie on a continuous curve, the points at high temperatures being in no case abnormal. Of the 33 points observed, 29 agree with the theoretical values within 1 per cent., and the other 4 within $2\frac{1}{2}$ per cent. The theoretical curve was plotted on the assumption that 11 per cent. of the γ-radiation, capable of penetrating the iron plate 0·6 cm. thick placed before the electroscope, comes from radium B. This result was kindly supplied me by Messrs. Moseley and Makower, who have been investigating the γ-radiation of radium B in detail. The radium B γ-rays affect chiefly the initial part of the curve, over which no measurements were taken.

The β-ray activity also decays at the theoretical rate at high temperatures (1150°) and low temperatures (200°) alike, and the amount of activity is unaltered with temperature. Of the 35 points observed, 2 are within 3 per cent., 2 within 2, and the rest within 1 per cent. of the theoretical values.

The rest of this paper deals with the behaviour of the active deposit inside sealed tubes containing radium emanation.

5. *Volatilisation of Radium C inside Quartz Tubes.*

A tube of clear quartz, 7·2 cm. long, diameter of section 0·5 cm., and wall thickness 0·04 cm., was filled with about 25 millicuries of emanation at a pressure of 20 cm. of mercury.

It gave a very uniform fluorescence on a zinc sulphide screen, which could be seen even in a fully lighted room when the screen was held in the shadow of the observer. The tube was then inserted in the furnace, so that one end was just inside, while the other end was in the centre. The hotter end was at 700°, and the cooler about 500°. After five minutes the tube was taken out, and its fluorescence on the screen again examined. The fluorescence was now almost entirely concentrated as a bright green spot not more than a couple of millimetres in diameter at the cooler end, while that from the rest of the tube could only just be seen in the dark room. The tube was then replaced in the same position as before, but reversed. After five minutes the whole of the fluorescence was now at the other (the cooler) end. The wrapping of 0·5 mm. lead round the tube did not effect any change in the position of maximum fluorescence. It must therefore be concluded that radium C is capable of complete volatilisation inside the tube at 700°.

This experiment has been repeated with the hotter end of the tube at different temperatures varying from 15° to 1000°. With increasing temperatures from 320°, the radium C shifts more or less completely to the cooler end of the tube, and the higher the temperature the more quickly is this accomplished. An exposure for half an hour at 320° is sufficient to produce the maximum change. Below this temperature the fluorescence is not continuous, but consists of bright and dark patches, the cooler half of the tube being always more fluorescent than the other.

The time required to produce a marked change in the fluorescence at these low temperatures is from two to three hours, and therefore makes it difficult to prove whether the radium C is itself volatilised, or whether it is produced *in situ* by volatilised radium B.

Quantitative results were also obtained by means of γ-ray measurements. Let A be the leak in divisions per minute when the cooler (and therefore more active) end is nearer the electroscope, B the leak when the activity has been driven by heat to the other end, so as to be about 7 cm. farther away from the electroscope, then the ratio A/B serves as a measure of the amount of radium C capable of volatilisation at a given temperature. For each temperature the leaks A and B were determined twice, so that the radium C was moved bodily along the whole length of tube four times. In the experiments, the results of which are summarised below, the tube was 22 cm. from the electroscope, and the side of the electroscope consisted of lead 1·8 cm. thick.

Temperature of hotter end ...	1000°	800°	700°	650°	600°	500°	450°	320°	15°
" cooler end ...	800°	600°	525°	400°	320°	260°	230°	150°	−80°
Ratio A/B (γ-rays)	1·70	1·72	1·71	1·72	1·62	1·49	1·42	1·26	1·06
Time required for maximum effect (minutes)	5	5	5	10	15	20	20	30	180

It was found experimentally that a shift of a point source of radium through a distance of 7·2 cm. (the length of the tube) under the conditions of experiment gave a value of 1·71 for A/B. Between 450° and 600°, therefore, a large and increasing percentage of radium C can be volatilised, while from 650° upwards the volatilisation is complete. The ratio A/B for β-rays at 650° is 6·6, a result to be expected when it is considered that, in addition to a mere distribution change, there is a large effect due to a change in the average path of the rays through the quartz. The γ-ray activity of the tube with the radium C concentrated at one end (the nearer, let us say), measured over a period of three hours in the cold, falls to the normal value to be expected if radium A, radium B, and radium C are in equilibrium at one end, and the rest of the tube contains emanation only. Experiments have also demonstrated clearly that from 450° onwards the radium C itself is volatilised and not merely grown from radium B.

It thus appears that at 650° radium B and radium C, and very probably radium A, are completely volatilised in quartz tubes. Radium B commences to volatilise at room temperature.

Results of a similar character have been obtained with tubes Nos. 1 and 2 described in the next section. For the former the ratio A/B (β-rays) at 700° was 2·78, at 500° 2·19, and at 350° 1·18. At 700° the ratio A/B for γ-rays corresponded to a total shift of the active matter from one end of the tube to the other. For the latter tube A/B (β-rays) was 1·29 at 700° although from its size and shape (it was a sphere, outer diameter 3 mm., of uniform wall thickness) so large a distribution effect is at first sight unexpected.

These results on volatilisation are entirely at variance with those of previous authors, who found that at temperatures of about 900°, 600°, and 1200°, radium A, B, and C respectively are completely removed from a platinum wire. No explanation of these discordant results need be attempted here, but the lack of agreement between the two sets of experiments is probably due to differences in pressure, and to the shape and nature of the surface on which the active material is deposited.

6. *Experiments with Radium Emanation.*

A series of experiments on the activity of the radium emanation at high temperatures, made in the beginning of the investigation, will now be described.

Two shapes of tubes were used. They are shown in fig. 1 as they appear after being sealed up. No. 1 was conical in shape, made of clear quartz, 1 cm. long, sectional diameter of narrow end 0·1 cm., and of wider 0·5 cm., wall thickness 0·03 cm. No. 2 was made of quartz, spherical in shape, of outer diameter 0·3 cm., and wall thickness 0·025 cm. Both tubes gave essentially the same results.

Tube No. 1, containing about 30 millicuries of emanation at a pressure of 16 cm. mercury, was mounted in the centre of the furnace, the broader end AB being nearer to the electroscope. The furnace was heated slowly, so that after one and a-half hours the maximum temperature (1150°) was reached. It was then kept at this temperature half an hour, cooled to 300° over an interval of 45 minutes, and then from 300° to 15° in about three hours. The β-ray activity was measured every minute. It was found that the β-ray activity increased continuously from room temperature to 600° no less than 25 per cent., decreased sharply between 600° and 700° to a value 9 per cent. greater than at 15°, and remained unchanged from 700° to 1100°, no matter how long the heating was continued. The tube was then cooled slowly in the furnace. The activity remained constant till 700°, increased rapidly between 700° and 600° to its old value 25 per cent. greater than at 15°, remained there till 300° was reached, and then fell slowly in the course of three hours to the room temperature value. These processes of heating and cooling were repeated several times. It was estimated that the critical temperature at which the sudden change in activity occurred was 650°.

FIG. 1.

Measurements of γ-rays in a similar experiment lasting five hours were also carried out. Details of the heating and cooling, with values of the leaks, are tabulated in Table I.

Table I.

Temperature of the tube.	Leak in divisions per minute.		
	Mean.	Highest.	Lowest.
Heated from 15° to 1000° in 1 hour	43 ·9	44 ·1	43 ·8
Cooled from 1000° to 300° in 20 minutes	43 ·9	44 ·2	43 ·6
Heated from 300° to 1000° in 20 minutes	43 ·7	44 ·0	43 ·6
Maintained at 1000° for 1 hour	43 ·8	44 ·0	43 ·6
Cooled from 1000° to 100° in 1 hour	43 ·6	44 ·2	43 ·4
Maintained at 500° for 1 hour	44 ·0	44 ·2	43 ·6
Cooled from 500° to 15°	43 ·8	44 ·2	43 ·4

The leaks are corrected, of course, for the decay of the emanation at room temperature during the period of measurement (0·75 per cent. per hour). These results show that the γ-ray activity is not affected by temperature to any appreciable extent.

The emanation tube (AB nearer the electroscope) was next supported exactly in the centre of the cross-section of the furnace tube and near one end of it. It was then heated for an hour at the highest temperature attainable at that point, and cooled slowly over an hour to 250° or 300°, β-ray measurements being made every two or three minutes.

The whole furnace was then turned round, the part CD of the emanation tube being now nearer the electroscope, and the experiment repeated. The tube was then pushed down the furnace cylinder, and the whole procedure given above exactly repeated. This was done for ten points along the furnace tube. Let a be the leak with the tube cold, b when the tube attains 300° after cooling from the highest temperature, and c when the highest temperature has been reached, then for different distances along the furnace tube (12·5 cm. long) the following results were obtained, the origin of length being the end of the furnace tube to which the broader end of the emanation tube is nearer, and a being put at 100 throughout.

Table II.

Distance (cm.)	3·7	5·0	6·0	6·3	7·5	7·7	8·0	8·5	9·3	10·5
AB nearest electroscope—										
a	100	100	100	100	100	100	100	100	100	100
b	167	141	143	125	108	108	102	102	84	75
c	121	111	110	109	108	108	107	106	95	93
Temperature at which c is measured	850°	1080°	1100°	1120°	1120°	1120°	1120°	1000°	1000°	800°
CD nearest electroscope—										
a	—	—	100	100	—	—	100	—	—	—
b	100	100	96	81	100	100	110	100	100	100
c	130	122	102	102	100	100	108	88	85	83

It was not convenient to measure all the a's, as this necessitated waiting three hours for the distribution to become normal again at 15°. When no measurement of a was made, b has been put at 100.

Consider just now only the b's and c's. At 7·5 and 7·7 cm. $b = c$, whether AB or CD is nearer the electroscope. For distances greater than 7·7,

$b < c$ with AB nearer,
$b > c$ with CD nearer.

For distances less than 7·5,

$b > c$ with AB nearer,
$b < c$ with CD nearer.

Leaks other than a, b, or c are not discussed, as experiment showed that their values depend entirely on the magnitude of a, b, and c.

The temperatures at various points along the furnace tube were next measured, when the hottest part in the centre was kept at various temperatures, from 200° to 1100°. The results showed that the hottest part of the furnace from 200° to 1100° was not in the centre (*i.e.* at 6·3 cm.), but at a point 7·5 cm., identical with the point at which $b = c$ in Table II. At 1100°, 2 cm. on either side of this point had a very constant temperature, but this 4 cm. of very constant temperature decreased to 1 cm. as the temperature fell to 300°. If, therefore, the centre of the active tube were not situated at this point, but, say, at 0·5 cm. on either side of it, it would have a constant temperature at 1100°. As this temperature is reduced, however, one end would tend to become hotter than the other, though the differences in temperature would be only of the order of 10 degrees. When the tube is placed at greater distances than 2 cm. from the centre, the difference in temperature between the ends, when the tube has been heated a long time at 1100°, is much smaller than it is when it has been cooled to 300°, owing to the way in which the furnace cools. Now it is a fact that radium C concentrates in the cooler end of a tube between 320° and 1100°, and the more easily the greater the temperature difference between the two ends. The results, therefore, for b and c of Table I receive a full explanation when this volatility is taken into account. Two examples are discussed:—

(1) Distance 6·0 cm., AB nearer.

AB is cooler than CD at 300° .... (*b*)
But has same temperature at 1000° ...... (*c*)
Therefore $b > c$.

With CD now nearer,

CD is hotter than AB at 300° .... (*b*)
But has same temperature at 1000 ...... (*c*)
Therefore $b < c$.

(2) Distance 10·5 cm., AB nearer.

AB is throughout hotter. The difference in temperature between AB and CD is less at 1000° than at 500°.
Therefore $b < c$.

With CD now nearer, same consideration applies as above, CD is cooler.
Therefore $b > c$.

It is still conceivable, however, that a real change of β-ray activity exists at high temperatures, but that it is masked by this relatively large distribution change.

At points 7·5 and 7·7 cm., however, $b = c$ no matter in which direction the emanation tube points towards the electroscope, so this supposition is entirely excluded. We therefore conclude that, betwen 300° and 1100°, there is no effect of temperature upon the β-radiation of the emanation.

In general, the order of results whether $a > b$, $b > c$, etc., depends not only on the length of the tube, and how it is placed in the furnace, but also on the winding of the furnace, and whether it is heated quickly or slowly. It is not at all difficult, even with the tube near the centre of the furnace, to obtain conditions whereby, on heating to 1100° and cooling to room temperature, the activity passes through two maxima and minima.

The author has been able to repeat all of the abnormalities in the activity of the emanation found by Engler, and to obtain even some which Engler himself could not repeat. Moreover, for every experiment in which the activity apparently increases when subjected to a temperature change, an experiment may be devised in which the activity decreases, and *vice versâ.*

7. *Partition of Homogeneously Distributed Activity.*

It still remains to explain why the leaks *a* and *c* of Table II differ, which correspond to the β-ray activities of the emanation tube at 15° and 1100° respectively. It may be seen from Table II that, when the tube is near the centre of the furnace, the leaks differ by a constant amount (8 per cent. approximately when AB points towards the electroscope, and about 3 per cent. when CD does). These differences may be explained by a consideration of the partition of radium C inside the tube between the walls and the contained volume. When an emanation tube has stood at room temperature for three hours, the partition of radium C has attained a steady state. The larger part of the active material is known to be on the walls, but a small part must be distributed throughout the volume of the tube. This partition gives the ionisation denoted by *a*.

Heating the tube uniformly beyond 650° volatilises radium B and C, so that the partition of radium C is changed. Prolonged heating at 1100° cannot effect the partition further. This gives the ionisation *c*. If, now, the tube be suddenly cooled to room temperature, by tipping it out of the furnace on to a cold porcelain plate, the volatilised products are precipitated entirely on the walls, and quite uniformly, as there is no reason, if the tube be properly cooled, why the products should concentrate at one end rather than at another. γ-ray measurements confirm this. This gives a third partition of radium C; let it be called *d*.

Each of these partitions gives a different ionisation effect due to β-rays, because, under ordinary conditions, the average path of the β-rays through the quartz depends upon the character of the partition. Consider, for example, these types of partition inside a sphere of uniform wall thickness (0·025 cm., say), and internal radius r (say, 3 mm.), mounted symmetrically with regard to the electroscope 30 cm. away. We are concerned only with the passage of rays through the hemisphere facing the electroscope. In partition *d*, the particles of radium C lie on a sphere of radius r.

Partition *c*, in which the radium C is distributed uniformly throughout the volume, may be approximately represented by a uniform distribution of particles of radium C on an ellipsoid of revolution about a major axis $2r$, the minor axes of length $2r''$ lying in a horizontal plane at right angles to the side of the electroscope through which the β-rays enter. Partition *a* may be represented by a distribution of radium C on a similar ellipsoid with minor axes $2r'$ $(r > r' > r'')$. If a section be now cut at right angles to the major axis, and the average distances through the quartz of lines joining all points for the circle and for the two ellipses to the electroscope respectively measured, it is found that the lines from the circle make the largest average intercept on the quartz and those from the ellipse corresponding to the ellipsoid of minor axis $2r''$ the least. Now what applies to this section applies to any section parallel to it, and therefore to the whole sphere.

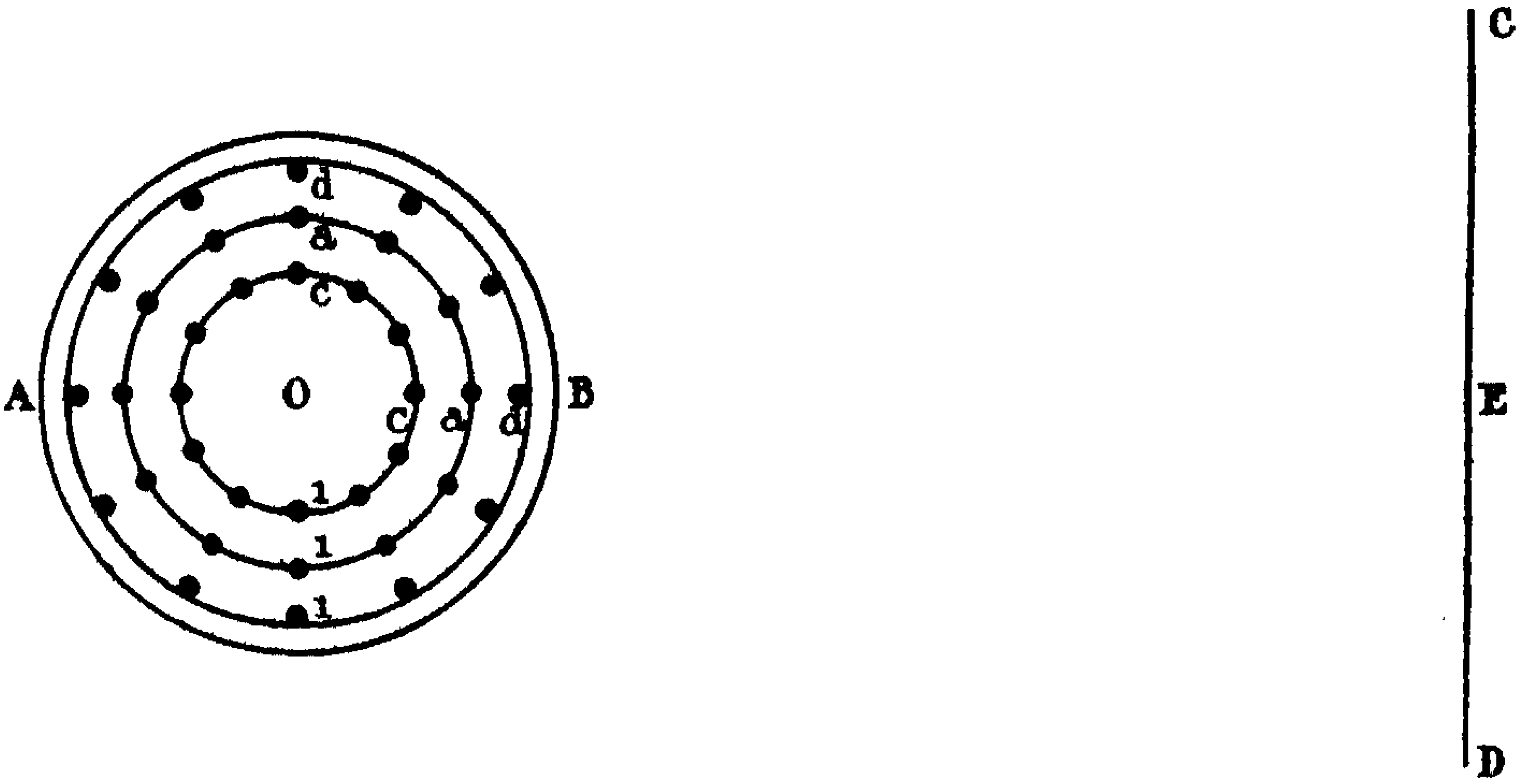

FIG. 2.

Thus, the particles of partition *d* are intercepted most by the quartz, and those of partition *c* least. From this it follows that for tube 2 ionisation *c* is the greatest of the three, and *d* the least.

In fig. 2 this is shown more clearly. AOB represents a horizontal section of the sphere through the centre, CD (mid-point E) the electroscope. The circles inside the sphere *a*, *c*, and *d*, represent the three partitions respectively. For convenience of making calculations the active matter is supposed concentrated on the circumference of the circle at 12 equidistant points. In the figure the inner diameter of the section is 3 mm., the wall thickness 0·25 mm., and the diameters of circles *a*, *c*, and *d*, are 2·2 mm., 1·5 mm., and 3·0 mm. respectively. CD at its distance from O corresponds to the breadth of the electroscope (7·5 cm.) at a distance of 30 cm.

From the point 1 of circle *d*, three lines are drawn to C, E, and D respectively, and the distance intercepted by the quartz in each case measured. This is done for all the points of one circle and for all three circles.

Putting now the sum of the 36 distances intercepted by the quartz as 100 for circle *a*, we get 83 for circle *c*, and 145 for circle *d*. This graphical method of solution is, of course, only rough. It takes no account, for instance, of scattering of the rays by the quartz, which must be not inconsiderable, but it serves to bring out the main result that the average path through the quartz is greatest for the particles on circle *d*, and least for those on circle *c*, and to give an idea of the magnitude of these differences.

As regards tube 1, a change of partition can only effect the ionisation when the axis of the tube points towards the electroscope, and here also $c > a > d$. When the axis of the tube is at right angles to the line joining the tube to the electroscope, it follows from geometrical observations that ionisations *a*, *c*, and *d* should be equal. This is what is found by experiment.

Repetition of the experiment by which ionisation *d* is obtained does not alter the value of *d*. Now, if the difference between *a* and *d* were due to an atomic change, one would expect that the difference would be proportional to the number of times the experiment had been carried out. If the tube be heated to temperatures below the volatilisation point of radium C (650°) instead of to 1000°, the difference between *d* and *a* is reduced. This is simply because partition *d* is the result of the precipitation on the walls of the tube of completely volatilised radium C. If the tube at 1000° be cooled *slowly*, the partition *c* is not affected until temperatures of about 300° are reached, though probably all of the radium C is solidified at this temperature. From 300° to 15° it commences to settle on the walls, and partition *a* results

For tube 1 (parallel to its axis, AB nearer to the electroscope)

$$a : c : d = 100 : 108 : 90,$$

and for tube 2

$$a : d = 100 : 84.$$

These results explain why Makower and Russ found that, although the activity of the emanation was less at high temperatures than at low, it decayed at the same rate. They were simply measuring the decay of the particles in partition *d* in one case and in partition *a* in the other. Both partitions are perfectly definite for any one tube, and therefore afford consistent results.

They explain also the result of Schmidt and Cermack (mentioned above,

p. 242), that, when the volatilised products were cooled quickly, the β-ray activity suddenly diminished. They attributed this to a sudden absorption of the products by the radium itself. It is due, however, to their precipitation on the walls of the containing tube and consequent alteration of the partition of radium C.

Summary.

(*a*) The effect of temperature upon the rate of decay, and the amount of β- and γ-ray activity, of radium emanation, active deposit, and radium C have been investigated. The results are entirely negative.

(*b*) Radium B and radium C, and very probably radium A, may be completely volatilised inside sealed quartz tubes at a temperature of 650°. Radium B commences to volatilise at room temperatures.

(*c*) All abnormalities of activity of β-rays obtained by previous authors, and by the author in this paper, can be completely explained on two simple grounds, a change of distribution and a change of partition, of radium C inside quartz tubes, produced by changes of temperature.

I take the opportunity of expressing my indebtedness to Prof. Rutherford for all he has done for me throughout the work.

BAKERIAN LECTURE:—*On the Variation of the Specific Heat of Water, with Experiments by a New Method.*

By H. L. CALLENDAR, M.A., LL.D., F.R.S., Professor of Physics at the Imperial College of Science, S.W.

(Received December 5, 1911,—Lecture delivered February 22, 1912.)

(Abstract.)

The question of the variation of the specific heat of water is so fundamental in calorimetry, and the results of different observers and different methods are still so discordant, that no apology is needed for the publication of fresh experimental evidence. The continuous electric method, which I carried out in conjunction with Prof. Barnes,* was specially designed to avoid the main sources of error of the older methods in which mercury thermometers and open calorimeters were employed. In this method, the rise of temperature of a steady current of water, heated by a steady electric current in its passage through a fine tube hermetically sealed in a vacuum-jacket, was observed with a differential pair of platinum thermometers. Errors due to lag, or to uncertainty of water-equivalent, or to evaporation or heat-loss in transference, were thus eliminated, and a higher order of accuracy was secured in the temperature measurements.

The results of the continuous electric method in the case of water showed a variation of specific heat amounting to less than one half of 1 per cent. between 10° and 80° C., with a minimum at 37·6° C., followed by a very slow and steady rise. The mean value from 0° to 100° C. agreed to 1 in 2000 with the experiments of Reynolds and Moorby by the mechanical method, and the values from 5° to 35° C. agreed to a similar order of accuracy with the experiments of Rowland. But the value at 80° C. was 1 per cent. lower than that found by Lüdin (Zürich, 1895), employing the ordinary method of mixture with an open calorimeter and mercury thermometers. Lüdin's results for the variation over the range 30° to 100° C. agreed more closely with the continuous electric method than those of any previous observers; but showed a minimum at 25° C., and a maximum at 87° C., which could not be reconciled with the experiments of Reynolds and Moorby on the mean specific heat from 0° to 100° C., or with the most probable reduction of Regnault's experiments between 110° and 190° C.

Within the last year the results of Lüdin have been almost exactly repro-

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* Callendar and Barnes, 'Phil. Trans.,' A, 1902, vol. 199, pp. 55–263.

duced by W. R. and W. E. Bousfield,* employing a Dewar calorimeter electrically heated by a mercury resistance. The mouth of the calorimeter was partially closed by an "obturator," maintained at a temperature 10° above that of the calorimeter, in order to minimise heat-loss due to evaporation, etc. The rise of temperature of the water in the calorimeter due to a measured supply of electrical energy was observed with mercury thermometers standardised to 0·01° every 5° C. Their results, like Lüdin's, showed a minimum at 25° C., and a maximum at 80° C., exceeding the value given by the continuous electric method by nearly 1 per cent. They attribute the discrepancy partly to uncertainty of the absolute value of the Clark cell in 1902, and partly to some heating effect of the current on the platinum-silver standard employed for the current measurement in the continuous electric method. In reply it may be urged that: (1) In default of satisfactory standards of comparison, the absolute value of the type of Clark cell employed was determined by direct experiment with a specially designed electrodynamometer by myself and Mr. King in 1898, and has since been verified to 1 in 14,000 by the independent evidence of Woolf and Waters.† (2) The platinum-silver standard was designed to carry 32 watts for a rise of temperature of 1° C. in a well-stirred oil-bath. Messrs. Glazebrook, Bousfield, and Smith, from their recent experiments,‡ are able to estimate the rise of temperature of this particular coil, under these conditions, as 0·95°, which agrees very well with my own experiments on which the design of the coil was based. Under the actual conditions of use, when carrying 20 watts as a maximum, the rise would probably not have exceeded 0·6° C., giving an increase of less than 1 in 5000 in the resistance, which was within the limits of error of the absolute determinations. (3) Uncertainty of the electrical measurements, if it existed, could not, in any case, explain the large discrepancy in the variation of the specific heat at 80° C., because the relative values of the specific heat were practically independent of the absolute values of the standards employed.

Assuming on the above grounds that the discrepancy must be due to some fundamental difference in the calorimetric and thermometric methods, it appeared desirable to verify the variation of the specific heat in the neighbourhood of 80° C., by an independent method. The "continuous mixture method," which I had already designed for experiments at higher temperatures, appeared peculiarly suited for the purpose, and was applied as follows to the question at issue. A steady current of air-free water at a measured temperature t_1 in the neighbourhood of 100° C., is passed through an arrangement of concentric tubes, called a "heat exchanger" (as indicated in the flow diagram annexed), where it loses some of its heat, emerging at a measured temperature, t_2, in the neighbourhood of 70° C. The current is then cooled to an accurately regulated temperature t_3, in the neighbourhood of 30° C., and is passed through the heat exchanger again as a cold current, abstracting heat from the hot current by conduction, without actual mixture, and emerging at a measured temperature, t_4, in the neighbourhood of 60° C. By a suitable arrangement of the flow tubes, the external heat-loss can be reduced almost to a vanishing quantity, without the employment of vacuum-jackets or elaborate precautions in lagging. The flow can be varied over a very wide range (20 to 1) without materially affecting the distribution of temperature; and, since the hot and cold currents are the same, a comparatively rough measurement of the current suffices for the determination of the heat-loss. The water equivalent of the exchanger is immaterial, provided that the conditions are steady, and there is no possibility of uncertain loss by evaporation, as in the case of an open calorimeter. The accuracy attainable is limited chiefly by the temperature readings, which were taken with platinum thermometers to 0·001° C., equivalent to 1 in 30,000 of the heat-exchange. Since the loss of heat by the hot current is equal to the gain of heat by the cold current, *plus* the small external heat-loss, the experiment gives the ratio of the mean specific heat from t_2 to t_1 (70°—100°) to the mean specific heat from t_3 to t_4 (30°—60° C.).

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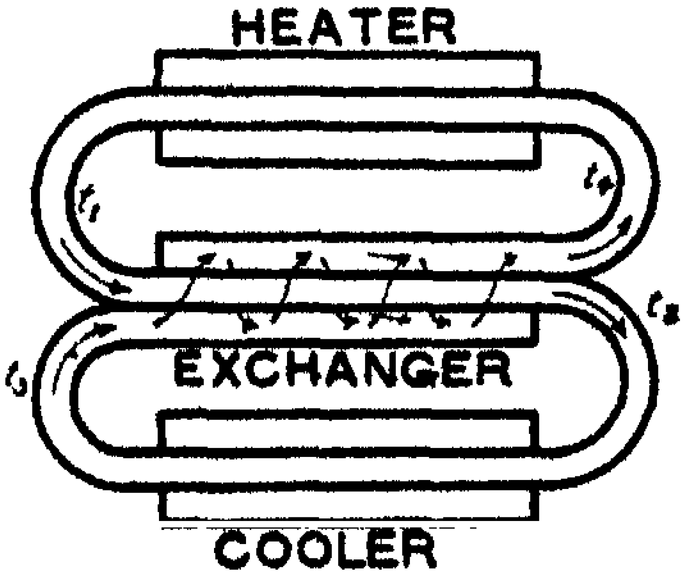
* 'Phil. Trans.,' A, 211, pp. 199–251.

† 'Bull. Amer. Bur. Stan.,' 1907.

‡ 'Roy. Soc. Proc.,' September, 1911.



The results of about 150 experiments by this method, in which the conditions as to flow and heat-loss were varied as widely as possible, were such as to confirm the continuous electric method over this range of temperature to less than 1 in 5000, whereas they differed from Lüdin's formula by more than 1 in 200.

An expression of the ordinary type $1+at+bt^2+ct^3+$ etc., as employed by Lüdin and other observers, cannot be found to represent the variation of the specific heat of water over the range 0° to 100° C. in a convenient and satisfactory manner. For this reason the results of the continuous electric method, when first published,[*] were represented by two or three very simple formulæ, covering different ranges of temperature. These have now been combined into a single continuous formula of a slightly different type, which is, in many respects, more convenient and accurate. The same formula also represents the most probable reduction of Regnault's results between 110° and 190° C., but may require modification over this part of the range when the continuous mixture method has been extended to higher temperatures. The formula for the specific heat s, at a temperature t, is as follows:—

$$s = 0{\cdot}98536 + 0{\cdot}504/(t+20) + 0{\cdot}0084(t/100) + 0{\cdot}0090(t/100)^2.$$

The terms in this formula are all small and positive, and can be calculated with sufficient accuracy for all purposes by the aid of a 10-inch slide rule, which is far from being the case if a formula of the Lüdin type is employed. The specific heat at 20° C. is taken as unity, and the scale of temperature t is that deduced from the platinum scale pt by the difference formula,[†]

$$t - pt = 1{\cdot}50\, t\, (t-100) \times 10^{-4},$$

as proposed at the British Association at Dover in 1899.

The corresponding formula for the variation of the total heat h, reckoned from 0° C. in terms of the same unit and temperature scale,[‡] is

$$h - t = 1{\cdot}1605 \log_{10}(t+20)/20 - 1{\cdot}1464(t/100) + 0{\cdot}42(t/100)^2 + 0{\cdot}30(t/100)^3.$$

The unit at 20° C. is the most convenient to adopt in accurate work for many reasons. In particular, the difference $h-t$ is always small and positive, in this case, between 0° and 100° C.; whereas, if the unit at 15° C. is adopted, the values of $h-t$ are negative over half the range.

Tables of s, and of $h-t$, calculated from the above formulæ, are given in the paper for each degree from 0° to 200° C. The absolute value of the mechanical equivalent at 20° C. is 4·180 joules per gramme-degree C. within the possible limits of error of the absolute measurements. The value at any other temperature is 4·180 s.

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[*] 'B. A. Rep.,' 1899.

[†] Recent experiments by Holborn and Henning ('Ann. Phys.,' 1911, vol. 35, p. 761) appear to show that this formula gives a better approximation to the absolute scale than has hitherto been supposed.

[‡] Dieterici's latest results ('Ann. Phys.,' 1905, vol. 16, p. 593) for the mean specific heat agree to 1 in 1000 (his limit of accuracy) with this formula over the range 0° to 100° C. But his results for the actual specific heat at t exceed those of Regnault when reduced to the same unit by 3 per cent. at 200° C., a discrepancy which appears to require further investigation.

The Spectrum of Comet Brooks (1911 c).

By Sir Norman Lockyer, K.C.B., F.R.S.

(Received December 14, 1911,—Read February 8, 1912.)

[Plate 8.]

On July 23 a Kiel telegram announced that the comet discovered by Brooks was of the tenth magnitude. During the next few weeks its faintness, combined with the bad state of the sky at Kensington, made it impossible to obtain any satisfactory observations.

On August 30—the comet having got considerably brighter by this time—an attempt was made to photograph its spectrum with the calcite prismatic camera. No trace of spectrum could be found on the plate. On August 31 an exposure of three hours was given, and two lines, evidently the carbon radiations λ 3883 and λ 4737, were feebly shown. Every available opportunity has since been taken of getting a photographic record with the same instrument. More or less successful photographs—the degree of success depending on the state of the sky on the various evenings—have been obtained on the nights of September 6, 11, 16, 20, 26, 28, and 30, October 4, 9, and 31. Between October 9 and October 31 the comet was not available, having changed in the interim from an evening object to a morning one.

The lines in the various photographs are all very broad and diffuse, and the reduced wave-lengths of the lines are probably only approximately correct.

On September 6 two weak radiations were found far in the ultra-violet region of the spectrum. The positions of these were approximately obtained by constructing a curve from the series of hydrogen lines in an excellent photograph of the α-Cygni spectrum taken with the same instrument. As the comet lines fall beyond this hydrogen series their wave-lengths had to be estimated by extrapolation.

In some of the later photographs these lines are much better shown, and other lines are seen when the sky conditions have been favourable. Thus a line whose position was at first estimated to be λ 3183 is well seen in the photograph of September 30 between the two ultra-violet lines previously mentioned. The values obtained from the curve for the latter lines were λ 3126 and λ 3369.

Subsidiary Bands between the Bright Radiations λ 3883 *and* λ 4737.

Whenever the cometary spectrum was photographed with any degree of success, three subsidiary bands were shown between the lines at λ 3883 and λ 4737. Their intensities are comparatively low and the lines are of such a diffuse nature that it is impossible to determine the wave-length of the middle of the lines with any great accuracy, especially as the lines are practically lost if any magnification is brought to bear on the spectra. The estimated wave-lengths, obtained by comparing the cometary spectrum with that of an iron arc photographed with the same instrument, are λλ 405, 421, and 436. With regard to the middle one of these it is very likely identical with the carbon band whose main head is at λ 4216.

In a paper* on the spectrum of Comet 1907 *d* (Daniel), Prof. Campbell gives a reproduction of the spectrum and a tabular list of lines which occur in it. There is a bunch of bright lines extending from λ 4020 to λ 4074, the mean position of the group being about λ 4047. There is little doubt that the broad diffuse line of the Kensington photograph is identical with the bunch of lines in Campbell's slit spectrum. Another well-marked, isolated, and sharply defined line in Campbell's spectrum is λ 4216, and this is probably the same line as is seen in the Kensington photograph, though in the latter it is of a very diffuse nature. The third line, approximately at λ 436, also appears to agree in position with another well-marked bunch of lines in Campbell's photograph. The strongest radiations in the latter are the carbon groups, λλ 3883, 4737, and these are the outstanding lines in the Kensington photographs. Thus, allowing for the difference in dispersion between the Lick and Kensington spectra, and for the fact that one was taken with a slit spectroscope, while the other was photographed with an objective prism, there seems little doubt that the spectrum of Comet Daniel, at the time Campbell photographed it, was practically of the same nature as that of Brooks' Comet during September and October.

Wave-lengths of the Ultra-violet Lines.

Assuming the middle of the strong radiation near λ 388 to be λ 3883, which is the head of the so-called cyanogen group, a comparison of the comet's spectrum with an arc spectrum of iron taken with the same instrument shows that the two stronger ultra-violet bands fall respectively on the iron lines λ 3100 and $\lambda \begin{cases} 3369{\cdot}62 \\ 3370{\cdot}87 \end{cases}$ as nearly as can be estimated. The mean values of the previous estimates of the cometary wave-lengths as obtained

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[*] 'Lick Observatory Bulletin,' No. 135.

(1) from an extrapolation curve, (2) by calculation from Hartmann's formula, were λ 3104 and λ 3359.

The position of the faint line between these two which comes in in the best photograph (September 30) has been estimated by comparison with the iron spectrum to be λ 316. The mean of the previous estimates was λ 3164.

The uncertainty of setting the middle of the strong diffuse line near λ 388 on its exact position amongst the iron lines in the comparison spectrum, combined with the very diffuse nature and comparative weakness of the ultra-violet lines, makes it impossible to give the wave-lengths of the latter with any great accuracy, and it will be well to adopt only three figures in the wave-lengths and refer to them as the lines λ 310, λ 316, and λ 337 respectively.

In order to determine, if possible, the origin of the ultra-violet bands, a series of comparison spectra was taken with the calcite spectrograph provided with a collimator. Long exposures on the spectrum of CO_2 have been made, but this has not given any clue to the origin of the cometary lines. Other modifications of carbon are now being tried.

Lines shown in the Various Photographs.

The following statement gives the approximate wave-lengths of the lines seen in the Kensington photographs:—

Date.	λλ.									
1911.										
August 31				3883				4737		
September 6	310		337	3883	405			4737		
„ 11	?		337	3883	405			4737		
„ 16	310		337	3883	405	421	436	4737	5165	
„ 20	310		337	3883	405	421	436	4737	5165	
„ 26	310		337	3883	405	421	436	4737	5165	5635
„ 28	310		337	3883	405	421	436	4737	5165	
„ 30	310	316	337	3883	405	421	436	4737	5165	5635
October 4	?		337	3883	405	421	436	4737	5165	5635
„ 9	(Poor photograph)			3883				4737		
„ 31	310		337	3883	405	421	436	4737	5165	5635

Amongst the photographs obtained from August 31 to October 9 inclusive no definite changes in relative intensity of the cometary lines were noticed. The difference in sky conditions on the various nights probably accounts for the fact that more lines were detected in some photographs than in others. On the other hand, the photograph of October 31, the first one taken after the comet had become a morning object, shows most decided changes in the relative intensity of some of the lines. Of the three subsidiary bands λ 405, λ 421, λ 436, the middle one was, in the series of spectra taken between September 16 and October 4 (the only spectra in which it was visible while the comet was an evening object), invariably the weakest of the three. In the spectrum of October 31, however, it is the strongest of the three. Another notable change was in the relative intensities of lines λ 3883, λ 4737. In the first series these two were of about equal intensity. In the later photograph λ 3883 is decidedly stronger than λ 4737. The ultra-violet lines λ 310 and λ 337, which are visible in nearly all the spectra taken when the comet was an evening object, are not seen in the spectrum of October 31. The changes mentioned can be seen by reference to the plate at the end of the paper.

Probable Origin of the Cometary Lines.

The identity of the cometary lines λλ 3883, 4737, 5165, and 5635 with lines of carbon or its compounds has previously been well established. With the object of determining the origin of the remaining lines, reference has been made to published records of laboratory spectra, especially those appertaining to carbon. No success has attended this search. The series of laboratory spectra recently taken here with the same object in view appears to throw no light on this point.

With regard to the origin of line λ 337, it may be said that there is a line at λ 336 given under the head of cyanogen by Liveing and Dewar, Eder and Valenta, and by Deslandres, but as the equally strong cyanogen band, the head of which is at λ 359, is apparently entirely lacking in the cometary spectra, it cannot be claimed that the identity of λ 336 with the cyanogen line of nearly corresponding wave-length has been established.

The reduction to wave-lengths and the discussion of the lines in the various cometary spectra has been undertaken by Mr. F. E. Baxandall, who has also taken part in the preparation of the paper. The series of photographs of laboratory spectra for comparison with the cometary spectra was taken by Mr. C. P. Butler. The wave-lengths of the ultra-violet lines were separately estimated both from an extrapolation curve and from Hartmann's formula by Mr. T. F. Connolly. The photographs of the comet's spectrum were taken with the 2-inch quartz-calcite prismatic camera by Messrs. W. Moss and T. F. Connolly.

DESCRIPTION OF PLATE.

The Kensington photographs shown on the Plate have been directly enlarged from the original negatives, the magnification being five-fold.

The upper illustration shows a comparison of the spectrum of September 30, when the comet was an evening object, and that of October 31, when it was a morning object. The chief differences between the two are referred to in the paper.

The lower illustration is a comparison of a portion of the Kensington spectrum of Comet Brooks, and the Lick spectrum of Comet Daniel* (1907 *d*), the latter having been taken with a slit spectrograph. There can be little doubt that the two spectra are nearly identical, bunches of individual lines in the Lick spectrum being represented in the Kensington spectrum by wide and diffuse lines.

* 'Lick Bulletin,' No. 135.

A Chemically Active Modification of Nitrogen, Produced by the Electric Discharge.—III.*

By the Hon. R. J. Strutt, F.R.S., Professor of Physics, Imperial College of Science, South Kensington.

(Received December 21, 1911,—Read February 8, 1912.)

§ 1. *Effect of Temperature on the Duration of Active Nitrogen.*

In the first paper (§ 2) it was mentioned that a stream of glowing nitrogen led through a tube cooled in liquid air glowed out with increased brilliancy, and then became extinguished. There is some ambiguity in the interpretation of this experiment, since the density of the gas is locally increased by cooling; and increased density may (and does) make the nitrogen expend its glowing power more quickly.

A hermetically sealed bulb containing rarefied nitrogen was excited by the electrodeless discharge. Allowed to expend itself at room temperature, the glow in this bulb was conspicuous for more than a minute. But if the bulb was immersed completely in liquid air immediately after excitation, and after 15 seconds withdrawn and examined, it was found to be quite dark. The glow was very brilliant as seen under the surface of the liquid air. This experiment proves that the glow-transformation really occurs more quickly the lower the temperature, apart from changes of density.

The same experiment was repeated, substituting boiling water for liquid air. Again the life of the glow was shortened, but this time its brilliancy

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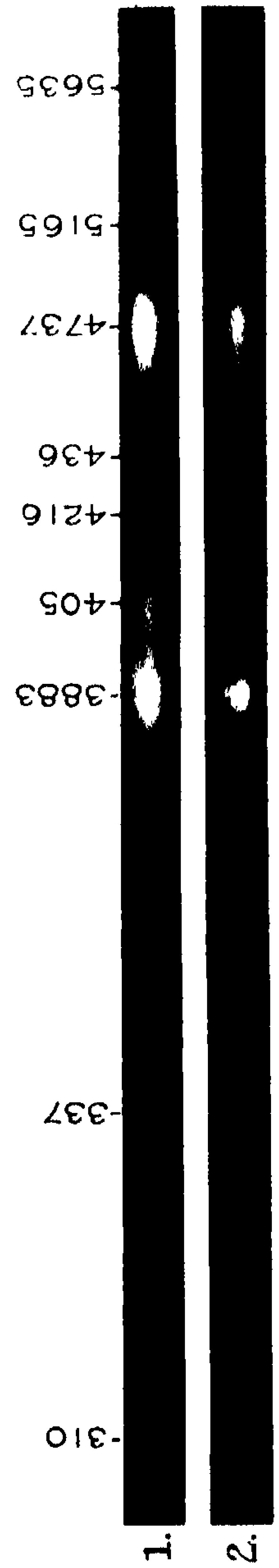
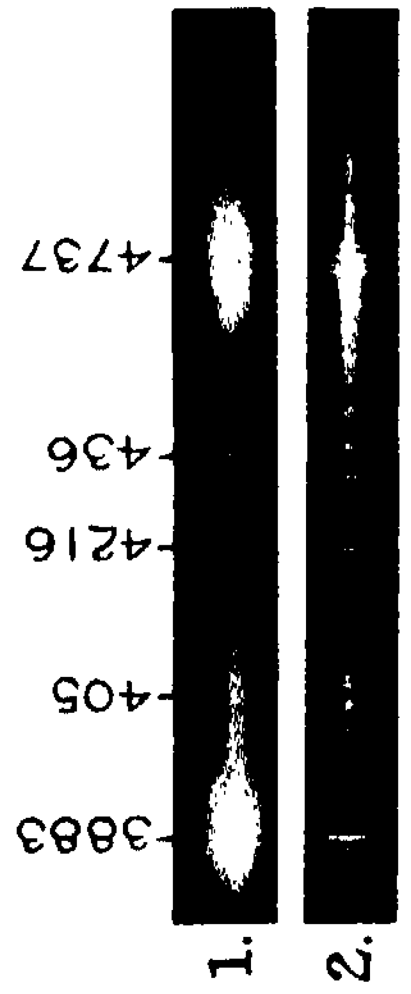
* Part I, 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 219; Part II, 'Roy. Soc. Proc.,' 1911, A, vol. 86, p. 56.

Lockyer. *Roy. Soc. Proc., A. vol.* 86, *Plate* 8.



Spectra of Comet Brooks (1911 c). 1. September 30 : 2. October 31.



1. Comet Brooks (1911 c), Kensington.
2. Comet Daniel (1907 b), Lick.

while it lasted was judged to be less than at ordinary temperatures. This corresponds very well with the results formerly obtained by the flow method. But now I feel able to offer more of an interpretation than was then possible. There are two phenomena to be reckoned with. One of these is a direct temperature effect on the glow-transformation. The other is a destructive effect of the walls of the vessel on the glow, also variable with temperature.

There are various reasons for believing in the existence of the latter effect:—

1. Certain substances, copper oxide, for instance, have been shown to be directly and immediately fatal to the glow, without themselves experiencing any change.* There is every probability that other solid surfaces, such as the glass walls, should, in a less degree, show the same effect.

2. When two similar glass bulbs are so thoroughly exhausted that no electrodeless discharge can pass, and then charged simultaneously with rarefied nitrogen and sealed off, the afterglow is about equally bright in each immediately after excitation. When a few seconds have elapsed, there is almost always a marked difference in luminosity between the bulbs. It is, in fact, impossible to get two bulbs which give the same rate of decay. As the initial intensity of glow is the same in each, this is most easily explained by supposing that the difference lies, not in the gas, but in the more unfavourable influence of the walls in the one case than in the other.

3. An experiment was made in which the glowing gas produced in one vessel was allowed to diffuse into two others, which were then shut off by a trap of sulphuric acid. The glow was initially of the same intensity in each vessel. The walls of one were wet with sulphuric acid, while those of the other were dry glass. The decay in the latter was much the more rapid. It cannot be doubted, therefore, that glass walls exercise some destructive action on the glow which sulphuric acid does not exert—at all events, in the same degree.

Admitting, then, that the walls produce a destructive effect on the active nitrogen analogous to that produced by cupric oxide, it is allowable to assume, as a working hypothesis, that this is increased by rise of temperature. The effect of cupric oxide, at all events, varies in that sense.

We are now in a position to interpret the observed effect of temperature on glowing nitrogen contained in a glass bulb. When cooled to −180° C., the effect of the walls in destroying the active nitrogen is, it is true, somewhat checked; on the other hand, the glow-transformation in the gas occurs more rapidly at that temperature, and the glow is given out in greater intensity and for a briefer period.

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* 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 226.

When the bulb is heated to 100° C., the destructive effect of the walls is increased, and this prevents the glow lasting so long as at ordinary temperatures, in spite of the fact that the glow-transformation is retarded. In the absence of the walls, the latter effect would make the glow feebler, but of increased duration. This, however, is not experimentally realisable.

We have it on the authority of Nernst* that no exception has been known to the rule that chemical change is accelerated by increase of temperature. The change from active towards inert nitrogen which is going on in the afterglow seems, therefore, to be unique in contradicting this rule.†

§ 2. *Effect of Density.*

Experiments on the duration of the glow with various densities of gas in the discharge vessel are difficult of interpretation, for two things are altered simultaneously—the conditions of discharge and the conditions of afterglow.

The effect of changed density can be examined to better advantage if the change is made when the gas is already glowing. The apparatus shown in fig. 1 was used to effect this.

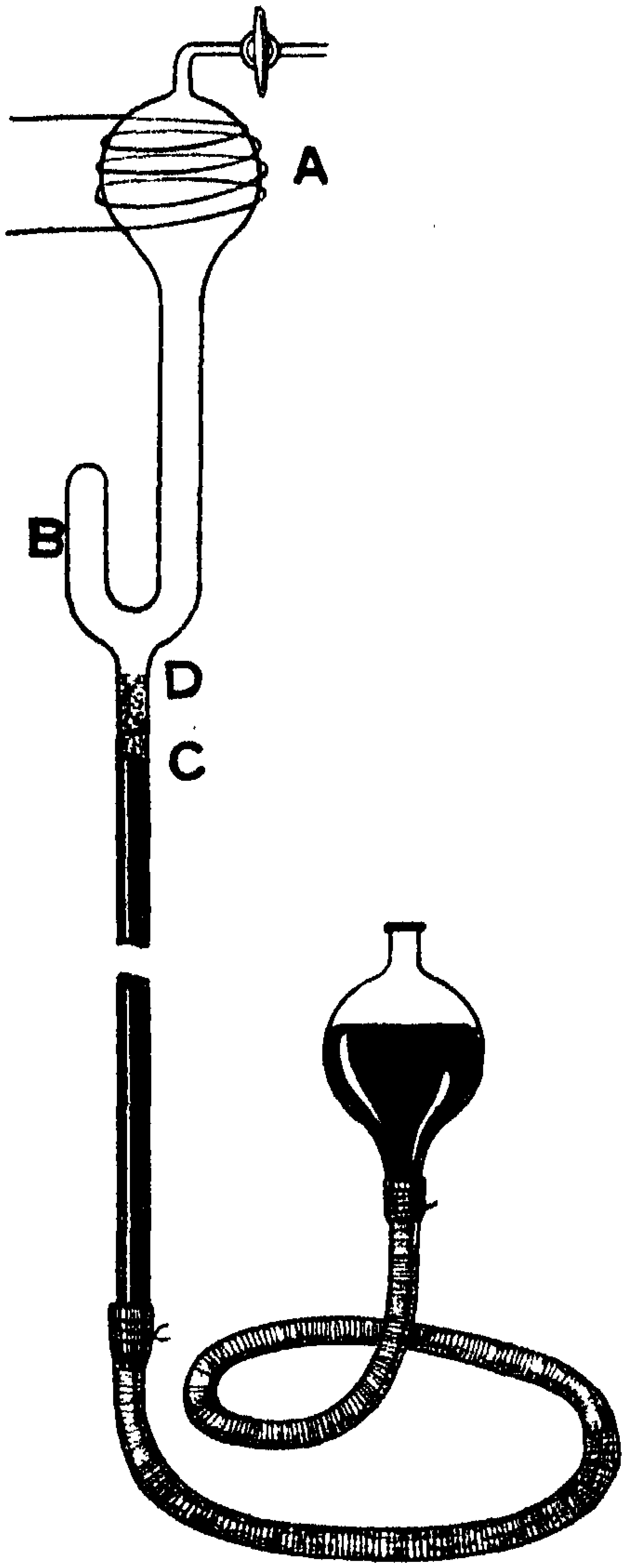

Fig. 1.

The electrodeless discharge passes in the vessel A. The afterglow diffuses almost immediately into the tube B. The mercury column C, covered with sulphuric acid* at D, can be raised so as to cut off the tube B from the rest of the vessel. The gas in B can be made to glow more brightly when compressed. In this condition it is more rapidly exhausted. If, after compression, the volume is kept constant, the glow gradually fades out. If it is *wholly* extinguished nothing is gained by compressing it further. But if any faint luminosity remains, it may be greatly increased by further compression. In this way the brilliance may be repeatedly restored by successive compressions. The process has been traced up to pressures of 4 cm. of mercury.

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* 'Theoretical Chemistry,' 1911 ed., p. 679.

† I desire to withdraw the too hasty suggestion made in Part I that the recombination of dissociated substances behaves in this way, and that this is a valid reason for regarding the active nitrogen as dissociated. It is necessary to distinguish between the effect of temperature in changing the rate of reaction and its effect in changing the condition of equilibrium to which the reaction tends (see Nernst, *passim*).

If, after compression to small bulk, the gas is again expanded, the luminosity is found to have disappeared, and tube B is now quite dark, though luminosity survives in the rest of the apparatus. If communication between B and A is again opened, a fresh supply of faintly luminous gas quickly diffuses in, and can be made to glow brightly by a second compression. This can be repeated several times without fresh excitation of the gas by discharge.

An alternative method of showing the effect of compression is more readily carried out, though less well adapted to a detailed study of the phenomena. In this case gas instead of liquid is admitted to drive the active nitrogen up to one end of the vessel.

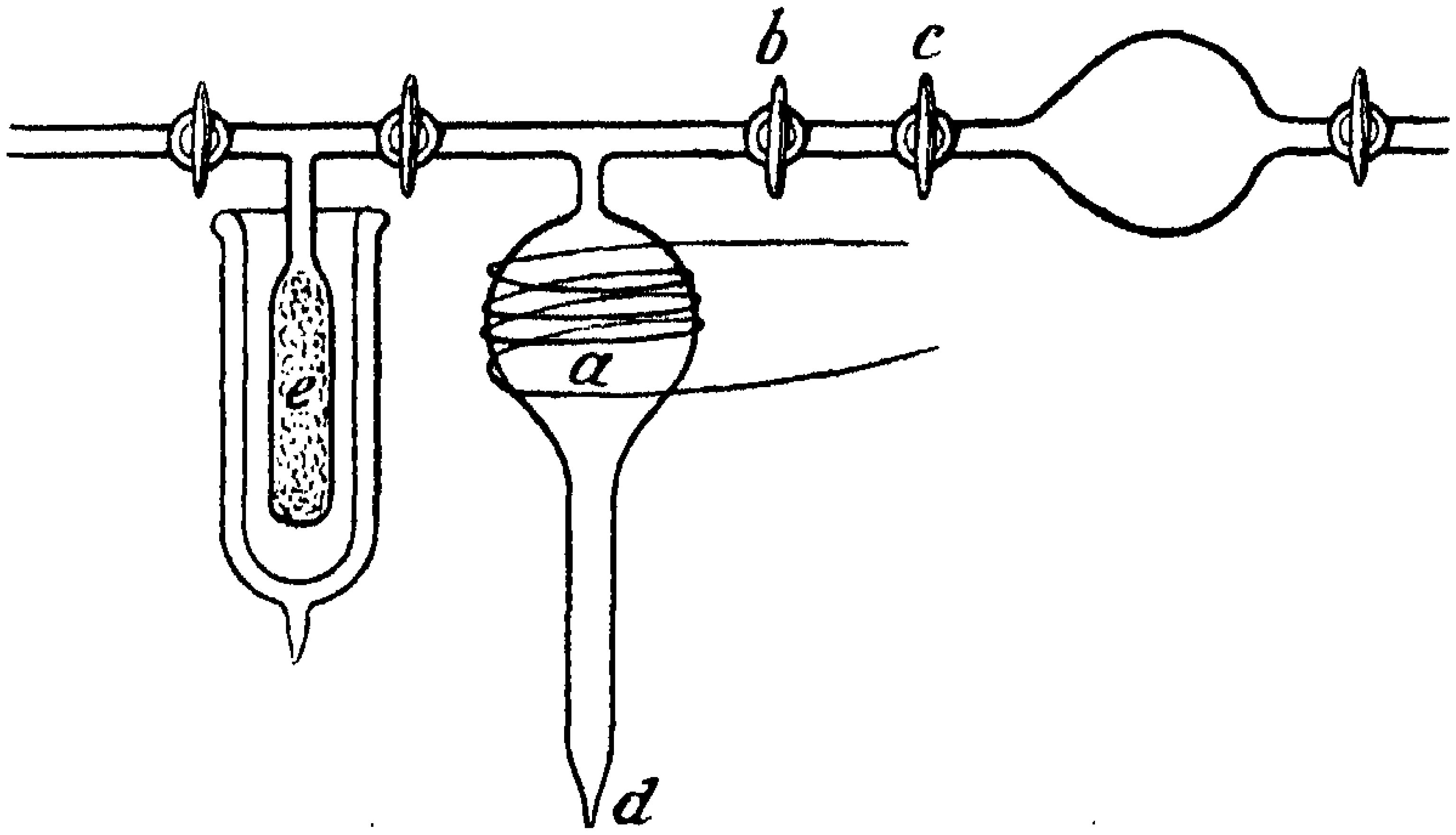

Fig. 2.

The electrodeless discharge passes in the vessel *a* (fig. 2), a bulb of 300 c.c. capacity. The afterglow is developed, and may be allowed to die down to a very low intensity. About 1 c.c. of nitrogen is then admitted from the space between the stopcocks *b* and *c*. This enters *a* and compresses the still glowing gas to the end *d*. A bright flash of luminosity is seen, due to the compression of the faintly glowing nitrogen already in the bulb.

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* When mercury was used uncovered, the glow was destroyed so soon as an attempt was made to compress it. This must be due to a destructive action of the mercury surface. I found formerly (*loc. cit.*, p. 225) that a mercury surface at rest had no effect on the glow. There must be some thin protective film on the surface of apparently clean mercury, which is broken up when it is moved.

To repeat the experiment, communication may be opened to the cooled charcoal in *e*, which quickly restores the degree of vacuum desired. The space between *b* and *c* is replenished from *f*.

The flash on compression is still more striking if *d* is immersed in an unsilvered vacuum vessel containing liquid air. In this way the intensity is increased by cooling as well as by compression.

In this form of experiment the nitrogen admitted merely acts as a piston compressing the glowing nitrogen, but not mixing appreciably with it. If the increase of pressure is made in such a way as not to cause a concentration of the glowing gas, no increased brightness is obtained. This may be realised in practice by gently admitting more nitrogen into a spherical bulb in which the glow has been generated, by means of a tube which projects into the centre, and is then provided with several jet-holes to distribute the entering gas uniformly in all directions.

The phenomena described are consistent with the following hypothesis:—Active nitrogen may revert to the normal condition in two ways—either by the action of the solid walls of the vessel, in which process no glow is emitted, or by its own spontaneous change, which *is* accompanied by the glow. This is analogous to what is known to happen in other gaseous reactions—the combination of oxygen and hydrogen, for instance. The change may be a volume one, with luminosity, as when the mixture is exploded; or it may occur at the surface of a solid catalyst, without luminosity, at comparatively low temperature.*

Although no quantitative measurements have been made, the experiments suggest that, with definite conditions of excitation, and if the effect of the walls could be eliminated, the time-integral of the intensity of the glow would be constant, unaffected by changes in temperature and density of the gas after excitation. The intensity of the glow is greatly dependent on these conditions, being increased by cooling or compression. But it is only increased at the expense of the duration.

§ 3. *Theoretical Inferences.*

It may be assumed that, where the action of the walls may be neglected, the visual intensity of the glow is a measure of the rate at which transformation is occurring. On this hypothesis, the compression phenomena described can give us valuable information as to the nature of the reaction from a molecular standpoint. If it is monomolecular, and the luminosity results from changes which can originate from a single molecule of modified nitrogen, then the rate of reaction will be proportional to the number of such systems in unit volume. The intrinsic luminosity should therefore increase on compression. But, if partial decay is allowed to occur at small volume, and the volume then restored, the amount of modified nitrogen remaining will be the same, and the glow will have the same brilliancy as it would have had after the same time interval, if no change of volume had been made at all. This is clear, without calculation, from the simple consideration that the transformation of each molecule of modified nitrogen is (*on this hypothesis*) *independent, and that the number remaining after* a given time cannot depend on whether the molecules have been brought close together or separated in the meanwhile.

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* See Bone and Wheeler 'Phil. Trans.,' 1906, A, vol. 206, p. 1.

We have seen, however, that this is *not* what is, in fact, observed. More rapid transformation occurs at high concentrations, and, on restoring the volume after considerable compression, the glow is found to have ceased, showing transformation to be nearly complete.

The observations, therefore, contradict the hypothesis of a monomolecular reaction. If we assume that the collision of two molecules of modified nitrogen is necessary to the reaction, then all is explained. Compression makes such collisions more frequent, and a given mass of modified nitrogen is more quickly transformed at small volume. The number of collisions is proportional to the square of the concentration; we may expect, therefore, very rapid increase of brightness when the volume is diminished beyond a certain point, by a piston moving with uniform velocity in a cylinder, as in the experimental arrangement. Since the active nitrogen is quickly used up at small volume, the luminosity will attain a maximum at a certain volume, the value of which depends on the velocity of the piston. On expansion after extreme compression, luminosity will be no longer visible.

The present experiments do not in themselves decide whether two or more than two molecules are concerned in the reaction. To do so, quantitative measurements of the law of decay would be necessary, and for this the action of the walls, which intervene in some way to cause a transformation without glow, would have to be eliminated. This action does not obscure the main features of the phenomenon, but it stands in the way of close quantitative scrutiny.

On general grounds, however, the reaction would naturally be regarded as bimolecular, in the absence of evidence that it is more complex.

§ 4. *Comparison with Prof. H. F. Newall's Experiments.*

Some very interesting experiments were described by Prof. H. F. Newall[*] in which he obtained brilliant luminosity from a sample of rarefied gas by compression after discharge. It was the study of his paper which led me to many of the above experiments, and any merit there may be in them must be largely credited to inspiration from this source. Prof. Newall was not able to specify precisely the nature of the gas with which his effect was obtained, or to reproduce it with certainty. He says: "I can only say that oxygen, with traces of nitrogen and SO_2, is the mixture I should begin with, if I wished to recover the conditions . . . ." The spectrum given out on compression he identified with the negative glow spectrum of oxygen.

Prof. Newall kindly came to see my experiments, and, while agreeing that the effect was one of the same class as that which he discovered, was unable to admit their identity. He is confident that his gas gave an afterglow with continuous spectrum, and that a discontinuous one was only developed on compression.

It seems best to state what I feel to be a difficulty. In my experiments compression has the effect of making the gas give out *more quickly* radiation which it will give out in any case. This is in sharp contrast with Prof. Newall's view of his effect. Again, my effect only occurs in pure nitrogen. Prof. Newall's effect, if it is really analogous, and gives an oxygen spectrum, should occur in pure oxygen. Many careful experiments with oxygen spectroscopically pure have convinced me that it does not develop a band spectrum when compressed after discharge. The spectroscopic test of purity in the case of oxygen is a severe one, for oxygen lines are easily outshone by impurities.

I cannot help thinking that something of the following kind may account for Prof. Newall's result. Suppose that he had nitrogen with some oxygen to begin with—such a mixture would give an afterglow with continuous spectrum. Passing the discharge undoubtedly sometimes causes an absorption of oxygen in such cases, as I have myself seen,[†] and the nitrogen remaining would show the peculiar afterglow spectrum, which would shine out brightly on compression. It seems to me that this spectrum might easily be mistaken for the negative glow of oxygen, particularly as the observations had to be made quickly, and the nitrogen afterglow spectrum had not been described at the time. The bands of these spectra in the visual region are in the following positions:—

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[*] 'Camb. Phil. Soc. Proc.,' 1895, vol. 9, p. 295.

[†] This may be due to formation of oxides of nitrogen and their absorption by alkaline matter on or in the glass surface.

Oxygen negative glow	5985, 5870, 5592, 5248.
Nitrogen afterglow	6252, 5804, 5407, 5054.

Certainly no other known gaseous spectrum would give so close a general resemblance to the nitrogen afterglow spectrum.

It may be added that many attempts to produce Prof. Newall's effect with different gaseous mixtures containing oxygen have failed. There is, indeed, a brightening of the nitric oxide afterglow by compression to one end of the tube, but the spectrum remains continuous.

§ 5. *Summary.*

(1) Active nitrogen emits its energy more quickly, and reverts sooner to ordinary nitrogen, if it is cooled. This is apparently a unique instance of a chemical change accelerated by cooling.

(2) If the glowing gas is compressed to small volume, it flashes out with great brilliance, and exhausts itself in so doing. This proves that the glow-transformation is polymolecular, *i.e.* that more than one molecule must take part in it.

(3) Active nitrogen may revert to ordinary nitrogen in two distinct ways. One of those is a volume change, accompanied by glow, the other a surface action of the walls of the vessel, without glow. This is analogous to the behaviour of oxy-hydrogen gas in its transformation to water, which may be a surface or volume effect, according to circumstances.

The Atomic Weight of Radium.

By Robert Whytlaw-Gray and Sir William Ramsay, K.C.B., F.R.S.

(Received December 27, 1911,—Read February 8, 1912.)

The essentials in determining the correct equivalent of an element are :—

(1) A pure compound of the element, and sufficient evidence of purity.

(2) An advantageous transformation, in which the weight of the element or elements combined with the one of which the equivalent is to be determined is as large as possible.

(3) If possible, no transference, and no operation which necessitates the use of reagents which can convey into the solution matter which may be adsorbed.

(4) A quantity sufficient in amount to make it possible with the balance at disposal to determine its weight to at least 1 part in 20,000.

(5) Resistant vessels, which will not themselves give up any material to the substance, and so make its purification difficult.

Determinations of the equivalent of radium have been made by Madame Curie, by Sir Edward Thorpe, and by O. Hönigschmid. Madame Curie's first determination, made in 1902, may be taken as avowedly only a rough approximation. Using 90 mgrm. of chloride, she found the atomic weight to be 225, assuming, no doubt with justice, that radium is a dyad.* Her second determination, of which a short account is given in the 'Comptes Rendus' for 1907, August 19, and a complete one in 'Le Radium,' translated in full in the 'Jahrbuch der Radioactivität,' 6, p. 38, employed the same method, viz., precipitation and weighing of silver chloride from a known weight of anhydrous radium chloride.

Madame Curie, in her earlier work, proceeded to the ultimate atomic weight progressively, raising the number from 140 to 146, then 174, then greater than 220, and in 1902 to 223·3; finally, with 90 mgrm., she obtained the figures 225·5, 226·0, and 224·2; mean, 225·2, which she regarded as accurate within a unit.

The method of crystallisation described in her later paper is merely indicated. A solution of radium chloride in hydrochloric acid was employed; 0·55 grm. was dissolved and evaporated, and deposited needle-shaped crystals. "The crystallisation was continued until almost all the salt had separated; the preparation was allowed to cool; the mother-liquor, containing very little salt (1 to 2 mgrm. in several cubic centimetres of the solution) was poured off. I carried out a large number of such operations, and always put together the separated portions. The salt was then divided into two parts, a first and a last portion." The samples were then tested spectroscopically for barium. She next added alcohol to a very concentrated aqueous solution until the salt was *completely* separated (italics ours). The liquid was then poured off and added to the mother-liquor. In this manner she obtained a certain improvement; it is not obvious, however, why an improvement was effected, if the salt was *completely* precipitated.

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* 'Comptes Rendus,' July, 1902, and 'Ann. Ch. Phys.,' 1903, vol. 30.

The silver chloride was filtered off, dried, ignited, and weighed on a balance sensitive to 0·05 mgrm. The amount taken was about 0·40 grm. After deducting the weight of the filter-ash, the figures 226·62, 226·31, and 226·42 were obtained, the values for Ag = 107·93, and Cl = 35·45 having been taken. Substituting 107·88 and 35·46, the figures are less by 0·09, or 226·53, 226·22, and 226·33; the mean of these is **226·36**.

Madame Curie comments unfavourably on crystallisation of the bromide; she states that the bromide, being much more soluble than the chloride, lends itself less easily to crystallisation, and that it is unstable, and changes very quickly; we shall see that these remarks are inapplicable. She also states that it is impossible to prevent a deposit of radium sulphate; this we have not noticed, having taken reasonable care to keep the vessels covered. She was also troubled by the impurities in the distilled water and the hydrochloric acid which she used, even though they were specially prepared and kept in platinum bottles. The silver chloride was always radioactive and luminescent; but Madame Curie states that it contained no radium detectable by the balance.

In his Bakerian Lecture for 1907,[*] Sir Edward Thorpe described experiments on the equivalent of radium. His raw material, placed by the courtesy of the Austrian Government at the disposal of the Royal Society, was "about 500 kgrm.," or, say, half a ton, of pitchblende residues from Joachimsthal. These residues were delivered by the Austrian Government to M. Armet de Lisle in Paris for preliminary extraction. Thorpe remarks: "The residues, as received by M. Armet de Lisle, were stated to have a radioactivity of about two and a half times that of uranium." This corresponds with Madame Curie's experience, for she wrote[†]: "La pêcheblende que nous avons analysée était environ deux fois et demi plus active que l'uranium." The total radioactivity of the 500,000 grm. received by M. Armet de Lisle was thus equal to that of

$$500{,}000 \times 2{\cdot}5 = 1{,}250{,}000 \text{ grms. of uranium.}$$

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[*] 'Roy. Soc. Proc.,' A, vol. 80, p. 298.

[†] 'Comptes Rendus,' vol. 127, p. 176.

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Thorpe received from Paris 413 grm. of mixed chlorides of barium and radium, the radioactivity of which was 560 times that of uranium. Hence the 413 grm. had a total radioactivity equal to that of

$$413 \times 560 = 232{,}000 \text{ grms. of uranium.}$$

Taking the radioactivity of pure radium chloride as equal to 1,800,000 times its weight of uranium, the figures result:—

Delivered in Paris ...... $\frac{1{,}250{,}000}{1{,}800{,}000} = 694$ mgrm. of pure radium chloride.

Received in London ... $\frac{232{,}000}{1{,}800{,}000} = 129$ " "

The method of separation of radium and barium followed by Thorpe was "substantially the same as that adopted by Madame Curie"; 9400 recrystallisations of the chlorides were carried out, towards the end in silica vessels. No details are given of the methods of crystallisation. The analytical process was also identical with that employed by Madame Curie, namely, precipitation of silver chloride from the dissolved radium chloride, acidified with nitric acid, subsidence, washing with distilled water six times, drying at 160°, and weighing on an assay balance sensitive to 0·1 mgrm. With the quantities used, an error of 0·1 mgrm. in the weight of the silver chloride made a difference of no less than half a unit in the atomic weight. The atomic weights used, moreover, viz., Cl = 35·45, and Ag = 107·93, have now to be corrected to 35·46 and to 107·88, hence the results of Thorpe's determinations are:—

I. 226·7; II. 225·6; III. 227·6.

The first two results were determinations with the same sample, which was recovered for the purpose; the last determination was made after mixture of another portion of 24 mgrm. with the first 64; this mixture was "repeatedly crystallised"; and the final results yielded a higher atomic weight. That the method employed was not particularly advantageous is shown by the discrepancy between determinations I and II, which, so far as weighings are concerned, should have differed by not more than 0·5 unit; that finality had not been reached is, we think, clearly shown by determination III, when, after repeated crystallisations, the atomic weight has been raised by one or by two units.

It is also stated by Thorpe that the bromide loses bromine, and eventually becomes insoluble in water, and that radium chloride, after standing in contact with glass, gives a faintly turbid solution; indeed, that all vessels are attacked by it, forming, apparently insoluble silicates. "A similar observation has been made by Madame Curie."

A new set of determinations has been made by O. Hönigschmid,* in which quantities somewhat exceeding 1 grm. were used. The method of purification was again that employed by Madame Curie and Thorpe, viz., repeated crystallisation of the chlorides from hydrochloric acid, and precipitation of the aqueous solution of the salt with alcohol. The equivalent was not altered after 50 such crystallisations and 13 precipitations with alcohol, and that material was regarded as pure, and employed in the final determinations. The method, too, was the same as that described, but in two cases the chloride of silver was reduced, and the weight of the silver ascertained. The mean result, taking Cl = 35·46 and Ag = 107·88, was 225·95; the extremes in seven determinations were 225·92 and 225·97.

Hönigschmid's work is undoubtedly very well done; the only doubt is whether his material was perfectly pure. It has been shown by Guye that it is impossible to separate potassium chlorate from potassium chloride, however many times the chlorate is recrystallised, owing to the existence of a solid solution. It will be seen in the sequel that the number obtained by Hönigschmid must be regarded as a minimum result.

Whilst these researches show the approximate atomic weight of radium, it cannot be said that the results must be accepted as final, for they are lacking in several of the conditions stated at the beginning of this paper. There is the possibility of contamination of the solutions with the reagents used; transference was necessary in all the experiments; both Madame Curie and Sir Edward Thorpe were troubled with insoluble deposits; and the accuracy of weighing was in the former case only 1 in 8000, and in the latter only 1 in 700. These disadvantages were absent from the method which we employed, viz., the conversion of radium chloride into radium bromide by heating it in a current of hydrogen bromide, and *vice versâ*; there was no transference, and only gaseous reagents were used.

By the courtesy of the Radium Corporation, 330 mgrm. of anhydrous radium barium bromide, containing about 70 per cent. of radium bromide, was placed at our disposal. This material, after being extracted from pitchblende, had been precipitated as sulphate, thus removing all heavy metals except lead, barium, and radium. The sulphates were delivered to us as bromides, into which they had been converted. The bromides received were dissolved in water and treated with sulphuretted hydrogen, which gave a small black precipitate; this was removed by settling and pipetting off the clear liquid, adding distilled water, again settling, and so on, until the precipitate had been thoroughly washed. Sulphuric acid was then added to the solution, so as to precipitate barium and radium. This precipitate was thoroughly washed by decantation; traces of alkalies, if present, were thus removed. All these operations were carried out in silica vessels. The washed and dried sulphates were next heated to redness in a mixture of carbon tetrachloride vapour and gaseous hydrogen chloride; they were thus converted into chlorides. A trace of iron appeared to be removed at this stage, and the residue became brilliantly white. The mixed chlorides dissolved completely in water, showing the absence of silica, and also of thorium, which volatilises as chloride under the circumstances. The Cornish pitchblende, however, contains only a few grammes of thorium per ton of uranium, and the maximum amount of mesothorium and radiothorium would therefore be vanishingly small.

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* 'Anzeiger der Akademie der Wissenschaften in Wien,' October 19, 1911; 'Sitzungsberichten der Akademie der Wissenschaften in Wien,' November, 1911.

These chlorides were next converted into bromides by heating to redness for some hours in a current of hydrogen bromide, and the exact amount was determined by conversion into chloride and back again into bromide in the following manner:—

The material was transferred without loss into a light silica capsule, resembling in form and capacity a No. 00 porcelain crucible, weighing on an Oertling's assay balance 1086·18 mgrm. A displacement of the milligramme rider on the beam of 1/50th of its length, corresponding to 1/50th of a milligramme, gave on the pointer-scale a difference of one division; greater accuracy could have been attained, but was not desired. The weights were Oertling's "assay silver weights."

It had been repeatedly proved that the weight of such a silica capsule remains absolutely constant even after it has been heated to redness for some hours in a current of dry gaseous hydrogen chloride, charged with the vapour of carbon tetrachloride; such a mixture of gases is easily made by use of a Kipp containing lumps of solid ammonium chloride and concentrated sulphuric acid. The gas, after passing a column of phosphoric anhydride, bubbled through a U-tube containing carbon tetrachloride. From this it entered a silica crucible of peculiar form, best illustrated by a figure which explains itself (fig. 1). The stopper is ground in, and it may be removed to introduce or take out the silica capsule. The silica apparatus was made by the Silica Syndicate, of Hatton Garden.

Heating in this mixture of gases removes all volatile chlorides; it also converts sulphates of the alkalies and alkaline earths into chlorides, and is by far the easiest way of effecting that conversion quantitatively. A very good equivalent was found for barium by conversion of a weighed amount of sulphate into chloride in this manner; the resulting chloride dissolved without a trace of residue. The radium bromide was thus converted into chloride; it was then reconverted into bromide by substituting for the hydrogen chloride plus carbon tetrachloride gaseous hydrogen bromide, made by bubbling hydrogen through bromine, passing the mixed gases through a red-hot silica tube charged with asbestos, and then through a column of phosphoric anhydride. The hydrogen bromide then entered the silica crucible; it converted the chloride into bromide. This operation takes about three hours.

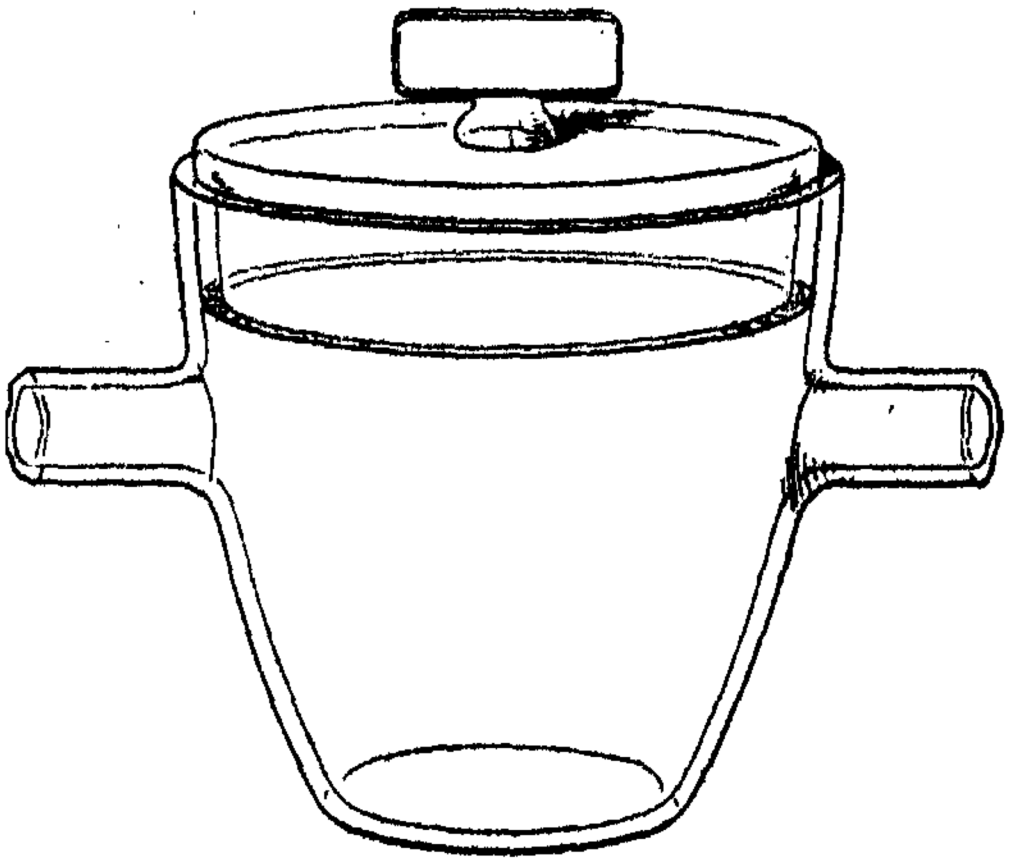

Fig. 1.

When the crucible cools, the mixture of bromides begins to shine with a beautiful sky-blue phosphorescence, increasing in intensity as it cools. The chlorides show a darker blue colour, and rapidly turn black. The silica capsule, while still fairly hot, was removed with platinum forceps and placed in a weighing bottle, arranged as a desiccator, with fragments of caustic potash. After standing for an hour it was weighed on the assay balance. Much has been said regarding the hygroscopic nature and the easy transformation of the bromide into insoluble substances, and there is some truth in the remarks. But in actual fact, it is not very hygroscopic. It is easy to transfer the capsule to the pan of the balance; and moisture is practically excluded by covering the capsule with a slip of mica during the operation of weighing. It stands to reason that the weight of the total moisture contained in the air imprisoned in the capsule is almost if not quite negligible; and even if withdrawn by the anhydrous bromide during the operation of weighing there is no reason why it should enter from the balance case. We have found, in effect, that under the circumstances the weight remains constant for more than an hour.

Having weighed the mixed bromides of barium and radium they were converted into chlorides by heating in a stream of dry hydrogen chloride, prepared as already described; this change is more rapid than the conversion from chloride to bromide. The capsule and contents were then weighed. A second conversion from chloride to bromide was made, and the weight again ascertained. The actual weights were as follows:—

Weight of capsule and mica cover	1086·18	mgrm.
„ mixed bromides, 1416·82 − 1086·18 =	330·64	„
„ „ chlorides, 1332·14 − 1086·18 =	245·96	„
„ „ bromides, 1416·82 − 1086·18 =	330·64	„

If x = weight of $RdBr_2$, and $y-x$ that of $BaBr_2$, and $297·32/386·24 = RdCl_2/RdBr_2$, and $208·29/297·21 = BaCl_2/BaBr_2$, then when $y = 245·96$,

$$(297·32/386·24)x + (330·64 - x)(208·29/297·21) = 245·96,$$

whence

$$x = 206·53 \text{ mgrm. } RdBr_2 \quad \text{and} \quad 330·64 - 206·53 = 124·11 \text{ mgrm. } BaBr_2.$$

Suppose that the chlorides had weighed 0·1 mgrm. less than 245·96, the difference in weight of the anhydrous bromide would have amounted to 205·08 instead of 206·53, or 1·45 mgrm. less. The balance can be trusted, however, to register one-fifth of this difference, or 0·3 mgrm. The percentage of radium bromide in the mixture is 62·5. This experiment is merely cited to show how it is possible to estimate the relative weights of radium and barium bromides in a mixture.

This mixture was dissolved in water in a silica capsule, and left to evaporate over night in a vessel containing phosphoric anhydride. In the morning a scum of carbonate had formed on the top. Addition of a drop of hydrobromic acid, made by saturating with hydrogen bromide water trebly distilled in silica and contained in a silica test-tube, dissolved the carbonate with effervescence to a clear solution.

The method of evaporating and crystallising was as follows:—The capsule containing the solution was placed in a flat-bottomed silica basin over a water-bath; evaporation proceeded until flat crystals began to form on the side of the capsule. These were pushed back into the liquid with a platinum wire, and evaporation was continued until a fair amount of crystals had separated. The solution was then allowed to cool, and the mother-liquor was removed with a small silica pipette of the shape and size shown in the figure into a silica capsule, also shown (fig. 2).

The crystals were re-dissolved in about six drops of water, which, like all the water used, had been distilled from silica, the steam passed through a short length of silica tubing, packed with silica wool and heated to redness. This prevented any carrying over drops of undistilled water. The water was kept in a little silica washbottle, entirely constructed of silica, without corks or rubber, from which it was easy to expel a single drop without splashing. All these operations were carried out in a glass photographic tray, covered by a sheet of plate-glass when it was not required to open it. In this way dust was practically excluded.

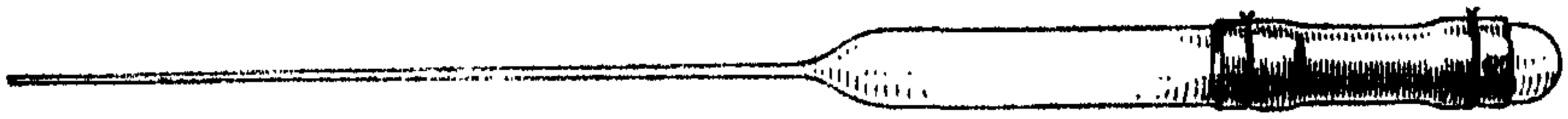

FIG. 2A.

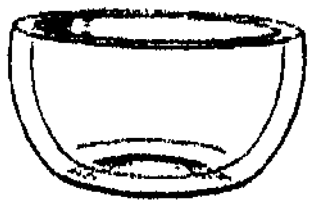

FIG. 2B.

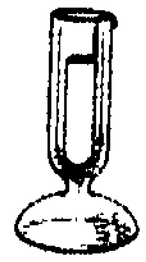

FIG. 2C.

The capsule with its six drops of water was heated in the silica basin over the water-bath until the crystals had dissolved. Two drops of hydrobromic acid were then added, and the evaporation continued as before; the second mother-liquor was placed in capsule 2; exactly the same manipulations gave mother-liquors 3 and 4.

At this stage a sample was taken from the residual crystals in the capsule, which may be called 5; it was transferred to a small silica bucket, weighing about 30 mgrm., contained in a holder of silica, as in fig. 2C, and it was heated to redness in the silica crucible (fig. 1) for an hour, in a current of hydrogen bromide. It was then transferred to a small weighing-bottle desiccator, and stored over potash for an hour. The bucket was then hung on the balance, and, after being weighed, the bromide was converted into chloride in the manner described, by heating for several hours in a current of dry hydrogen chloride; it was then cooled in the desiccator and weighed. It was then re-converted into bromide by heating it in a current of hydrogen bromide until weight became constant. The first weighing as bromide was rejected.

The weights are as follows:—

Weight of chlorides	0·42188	mgrm.
„ bromides	0·55082	„
Difference	0·12894	„

The atomic weight, calculated by the equation

$$0{\cdot}12894x = (159{\cdot}84 \times 0{\cdot}42188) - (70{\cdot}92 \times 0{\cdot}55082),$$

where 159·84 and 70·92 are respectively Br_2 and Cl_2, is 220; the percentage of radium bromide in the mixture of bromides, on the assumption that the atomic weight of radium is 226·4, has thus been raised from 62·5 to 94·4 per cent.

It is advisable here to introduce a short description of the balance, which, though essentially similar to that already described by us,* was slightly modified to suit the new requirements. In the experiments on niton, the measurement of a very small difference in weight (about 1/1000 mgrm.), with an accuracy of the order of 2 per cent., was required; but in the present work such an extreme sensibility was not necessary, although a much greater percentage accuracy was essential. The instrument was accordingly modified, so as to carry a much greater load, and the beam was made of a very rigid form. The design is shown in the diagram (fig. 3).

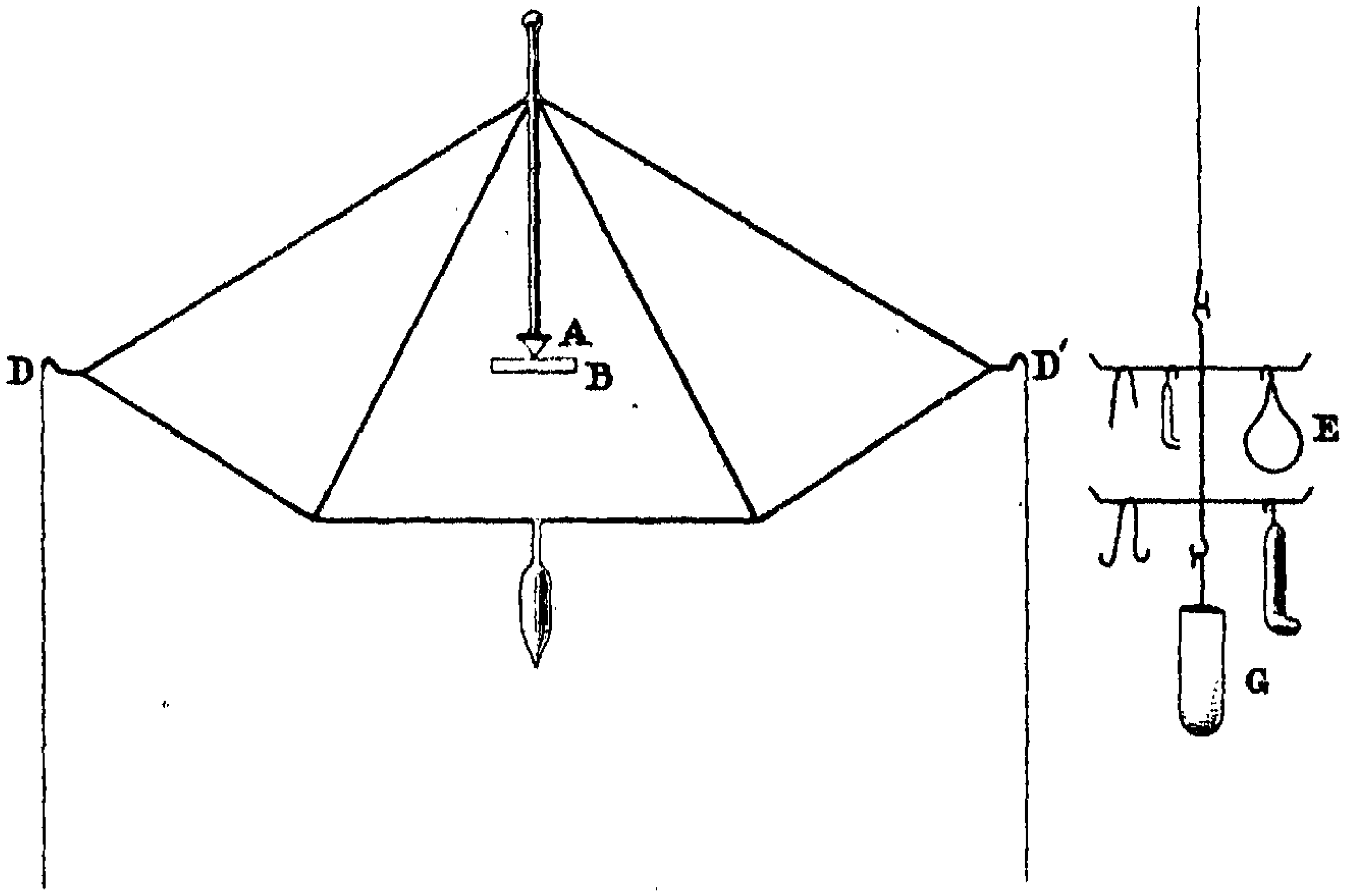

Fig. 3.

A is a central compound knife-edge, consisting of two small silica prisms, resting on a plate B of polished quartz. The arms carried two silica fibres at DD′, sealed on so that the points of attachment were as nearly as possible in the same plane as the edge A. The fibres terminated in hooks supporting a small framework of silica, on which the vessel to be weighed, the weights, and the counterpoise-bulb were suspended. The air-tight case and the attachments were similar in all respects to those described by Steele and Grant, and need no special mention. Previous experience with the more sensitive balance showed the importance of weighing at low pressure, in order to avoid air-currents produced by temperature changes when the case is suddenly filled or evacuated. This restriction of the range of pressure set a limit to the weight which could conveniently be applied by the counterpoise-bulb, and necessitated the use of a set of weights, for weighings of high percentage accuracy. The balance was therefore constructed so that its constant load was made up of: (*a*) the counterpoise-bulb; (*b*) the pan or bucket; (*c*) the weights, consisting of silica rod or open tube in the form of hooks, making together a weight of about 24 mgrm.; these [(*a*), (*b*) and (*c*) together] were balanced by a single counterweight of quartz suspended from the opposite arm of the beam. The bulb had a capacity of 158·04 cu. mm., and at 15° and 760 mm. pressure it displaced 0·1937 mgrm. of air; hence a pressure change of 1 mm. is at this temperature equivalent to an alteration of weight of 0·000255 mgrm.

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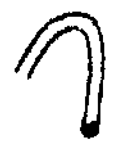
* 'Roy. Soc. Proc.,' A, vol. 84, p. 538; see also Steele and Grant, *ibid.*, A, vol. 82, p. 580.

The weights ranged from 20 mgrm. down to 0·1 mgrm. and were approximately adjusted on a delicate assay balance to within 1/100 mgrm.; an operation which, on account of the volatility of silica at its melting-point, is fairly easy. The pieces were constructed of different shapes so that they could be readily distinguished from one another. The smaller weights were made of fine silica capillary tubing, open at one end. The accurate comparison of the weights with one another was carried out in the micro-balance itself with the help of the counterpoise-bulb E. One of the 0·1 mgrm. pieces was first weighed against the bulb; this necessitated a change of pressure of about 400 mm., and care was taken to eliminate errors due to temperature changes and consequent air currents. The true value of the 0·1 mgrm. weight being known, it was easy to standardise the other two 0·1 mgrm. weights, and by successive replacement, all the pieces in the set. The values of the silica weights were thus determined in terms of the air displaced by the bulb; and this was known with a high degree of accuracy, probably to 1 part in 2000; but for our purpose an error in the standard was of course immaterial.

It will be clear from what has been said that since the balance was constructed for a constant load, weighing was always carried out by substitution, and the weights and object to be weighed, as well as the bulb, were always on the same side of the balance beam. The small object was placed in the bucket G, and weights were then removed until equilibrium was nearly restored; exact balance was attained by closing the case and varying the pressure until the spot of light on the scale had been brought back to the null-point. Thus the weights served as a coarse, and the counterpoise-bulb as a fine adjustment.

Although a knowledge of the relative values only of our weights was important, it should, perhaps, be pointed out that the standard weight calculated from the air-displacement of the bulb is practically the same, whether the bulb is vacuous or contains air. A vacuous bulb, counterpoised in a vacuum, is balanced by its own weight of silica at the opposite end of the beam. In air the silica of the bulb and the silica balancing it are buoyed up equally, and the weight turning the beam is the weight of air equal in volume to the internal volume of the bulb. If the bulb contains air, and is balanced in a vacuum, the silica at the opposite end of the beam balances the silica of the bulb as well as the air in it. This excess of silica is, however, of so small a volume that the weight of air which it displaces is negligible, and in consequence the buoyancy of the bulb is hardly diminished from what it would have been had the bulb been vacuous.

Before the balance was used a considerable amount of time was spent in testing it. The zero-point was found to be perfectly constant. Without the counterpoise-bulb no change in zero was detectable with large changes of pressure within the case. The sensibility was such that a deflection of the zero-point by 1 scale-division corresponded to 0·000014 mgrm. The weights were calibrated three times, and the annexed table shows their value and the method of entering them in our note-book.

Weight.	Face value.	True value.	Weight.	Face value.	True value.
	mgrm.	mgrm.		mgrm.	mgrm.
	2	2·01955		0·2	0·20535
	1	1·01645		0·2	0·19034
	1	1·00776		0·1	0·13576
	0·5	0·50082		0·1	0·10787
	0·5	0·49243		0·1	0·11004

For calculating the air-displacement of the bulb, the formula given by Steele and Grant was used, viz.:—Change in weight of air displacing bulb $= V\sigma_0 T_0/P_0 \, . \, (P_1/T_1 - P_2/T_2)$, where V is the volume of the bulb; σ_0 the density of air at normal temperature and pressure, T_0 and P_0; P_1 and T_1 are the pressure and temperature of the air in the case when the beam is unloaded; and P_2 and T_2 when the beam is loaded. The expression

$V\sigma_0 T_0/P_0$ is a constant for the bulb, and in our experiments had the value 0·07340.

In comparing the weights of substances of density different from that of quartz, a correction has to be made for the variation of buoyancy of the substance itself, as the temperature and pressure change. If the substance is denser than silica, which was the case in our experiments, the change of air-displacement with pressure and temperature is of opposite sign to that of the counterpoise bulb. Knowing the density of the substance weighed, the correction can be readily calculated. If x represents the apparent change of weight per milligramme per atmosphere undergone by the substance when the air in the balance-case is at 0° C., then x is equal to the difference between the alteration in buoyancy of 1 mgrm. of quartz and the substance per atmosphere at 0°. If Δ_Q = the density of quartz, and Δ_S = the density of substance, and σ_0 = the density of air at 0° and 760 mm., then $(1/\Delta_Q - 1/\Delta_S)\sigma_0 = x$, from which x can be calculated. If the density of the substance is unknown, the value of x can be determined experimentally, and since Δ_Q and σ_0 are known, Δ_S can be calculated. To determine x the counterpoise-bulb is removed from the balance and replaced by a counterweight. After placing a known weight of substance in the pan the beam is exactly balanced by adding weights and small fragments of silica fibre. The shift of the zero-point for a known pressure-change is then determined, and the temperature measured. The substance is then removed, the counterpoise-bulb replaced, weights added to restore equilibrium, and the change of pressure necessary to cause the same zero-shift over the same part of the scale measured. In order to determine the magnitude of the vacuum correction of any substance of unknown density, it is therefore only necessary to determine x per milligramme per atmosphere at the mean temperature of the weighings, and since in most cases x is small, a slight error in its value has no important influence on the results.

To illustrate how x has been measured, and how an approximate value for the density of a substance can be arrived at by this method, we give the results of two experiments, one with very pure anhydrous radium chloride, and the other with the anhydrous bromide :—

Radium Chloride.—1·818 mgrm. of anhydrous salt placed in the bucket was found to cause a deflection in the zero-point corresponding to 39·4 divisions when the pressure was changed by 760 mm. at a temperature of 16·85°. The average value of one scale-division at this part of the scale was found to be 0·00001414 mgrm.; hence the change of buoyancy per atmosphere = $39{\cdot}4 \times 0{\cdot}00001414 = 0{\cdot}000557$ mgrm. at 16·85°, and at 0°,

$0{\cdot}000557 \times 289{\cdot}85/273 = 0{\cdot}000591$ mgrm. The density of the silica from which the balance beam was made proved to be 2·197; the density of air at 0° and 760 mm. is 0·001293. Hence,

$$(1{\cdot}818/2{\cdot}197 - 1{\cdot}818/\Delta_S)\,0{\cdot}001293 = 0{\cdot}000591 \text{ mgrm.},$$

and $\Delta_S = 4{\cdot}91$. The vacuum correction per atmosphere per milligramme radium chloride is, therefore, at 16·85°, $0{\cdot}000557/1{\cdot}818 = 0{\cdot}000306$ mgrm.

By similar measurements, the density of anhydrous radium bromide was found to be 5·78, and the vacuum correction per milligramme per atmosphere at 18° equals 0·000342 mgrm. These values for the densities must, of course, only be taken as approximations.

To return to the fractionations. The five fractions were next treated in the following manner:—The contents of 2 were evaporated to crystallising point and the liquor transferred to 1 with the silica pipette, being added to the liquor already there. Similarly, the contents of 3 were evaporated and crystallised; its liquor was transferred to 2; the contents of 4 were treated similarly, and the liquor transferred to 3. The crystals in 4 were then dissolved in water, and the solution was transferred to 5; 4 was then washed three times, each time with a drop of water; and these washings were also transferred to 5. Capsule 4 was now empty; it was placed in position 1; 1 now became 2, 2 became 3, and 3, 4. The liquor in 2 was evaporated to crystallising point and cooled. Its liquor was transferred to the empty 1. The same process was repeated with 3, 4, and 5, their liquors being transferred to 2, 3, and 4. This constituted one "round."

After two such "rounds," a sample was taken for determination of equivalent. Weight of chlorides = 1·5830 mgrm.; of bromides = 2·0537 mgrm.; atomic weight = 228·2. It was suspected at this stage that some reaction must have taken place between the phosphoric anhydride through which the hydrogen bromide passed before entering the silica crucible, whereby a volatile phosphorus compound might have been formed, for it was noticed that on the lid of the silica crucible there were whitish spots. On dissolving this deposit off the lid with nitric acid a distinct yellow precipitate was formed with ammonium molybdate. The apparatus for preparing hydrogen bromide was therefore altered, so that the hydrogen was dried with pentoxide before bubbling through the bromine bottle; and the mixture of gases, after passage over red-hot asbestos, entered the silica crucible containing the radium bromide. In this way all danger of contamination of the bromide with phosphorus was avoided. Contamination with a phosphate would tend to raise the equivalent of radium, and might explain the high number obtained.

Recrystallisation was proceeded with until eight "rounds" had been achieved, and a sample was removed (1). The contents of capsule 5 were then dissolved in water to which a drop of hydrobromic acid had been added, and evaporated to crystallising point; it was arranged that only a couple of drops of mother-liquor remained with the crystals. This process was repeated, and a sample of these crystals was removed (No. 2). Again the crystals were redissolved as before, and a new crop obtained; this was repeated, and a sample of this crystallisation (No. 3) was preserved. A similar process, three times repeated, yielded sample 4, and a further crystallisation yielded sample 5. One more crystallisation gave sample 6, and one more, sample 7.

Samples 1 and 2 were reserved. Samples 3 and 4 gave the following figures:—

	Weight of bromide.	Weight of chloride.	Loss of weight.	Atomic weight.
	mgrm.	mgrm.	mgrm.	
Sample 3..................	1·50117	1·15474	0·34640	225·48
„ 4..................	0·36910	0·28400	0·08510	225·90
„ 5..................	Was accidentally spilt, so that no data are available.			
„ 6..................	2·85262	2·19586	0·65676	226·40

This sample was transferred to a silica capsule, and the weighing-tube was washed out and re-weighed, in order to see that its weight had not changed.

The sample was then replaced, with small loss, some fragments of bromide being impossible to remove from the capsule. The ratio was again determined.

	Weight of bromide.	Weight of chloride.	Loss of weight.	Atomic weight.
	mgrm.	mgrm.	mgrm.	
Sample 6 repeated......	2·76084	2·12492	0·63592	226·25
	After a second transference the figures were—			
„ „	2·61099	2·00988	0·60110	226·35
	After a third transference—			
„ „	2·43281	1·87275	0·56006	226·35

This sample, it was thought, might have become contaminated with dust, leaving a siliceous residue on ignition; any unchangeable matter would have raised the atomic weight; the presence of any other impurity, non-volatile in hydrochloric or hydrobromic acid, but changed to chloride or bromide by their action, except thorium and uranium, would have lowered the atomic weight. The sample was dissolved in two drops of the purest "silica" water, and any possible impurities allowed to settle in a silica tube; it need hardly be said that no sediment was visible. The clear liquid was removed with a silica pipette, transferred to the weighing-tube, and saturated with gaseous hydrogen bromide. Radium bromide was precipitated in crystals, and the mother-liquor was removed with a silica pipette. The crystals were then dried and heated in hydrogen bromide until the weight became constant; they were then transformed into chloride, and again weighed.

	Weight of bromide.	Weight of chloride.	Loss of weight.	Atomic weight.
Sample 7..................	mgrm. 2·36062	mgrm. 1·81711	mgrm. 0·54351	226·45

Samples 1, 2, and 3 were next united, so as to check the earlier values; it will be remembered that sample 1 had been reserved.

	Weight of bromide.	Weight of chloride.	Loss of weight.	Atomic weight.
Samples 1, 2, and 3 ...	mgrm. 2·91458	mgrm. 2·24144	mgrm. 0·67302	225·20

The sample was then converted from chloride to bromide.

Weight of chloride.	Weight of bromide.	Loss of weight.	Atomic weight.
mgrm. 2·24113	mgrm. 2·91415	mgrm. 0·67302	225·17

Knowing the value for samples 1, 2, and 3 together, and knowing the value for 3, the value for samples 1 and 2 together was calculated. The facts may now be stated thus:—

Samples	1 and 2	gave the atomic	weight by	calculation......	224·56
„	1, 2, and 3	„	„	„	225·19
„	3	„	„	„	225·48
„	4	„	„	„	225·90
„	6	„	„	(mean of 4)	226·34
„	7	„	„	......	226·45

The fractionation and rejection of 0·07 mgrm. of bromide between 6 and 7 has not materially altered the figure; it appears fair, therefore, to adopt the mean of samples 6 and 7 for the final atomic weight; this then becomes **226·36**.

This figure confirms Madame Curie's results, and is at variance with Hönigschmid's. The special interest in these determinations of atomic weight is that, as pointed out by one of the authors in his Presidential Address to the British Association, it affords for the first time a basis for approaching the difficult question of the ancestry and descent of the elements.

Assuming, first, that radium is the great-grandchild of uranium; second, that the only concomitant of the disintegration of these elements is helium; third, that each atom of uranium, during its change into uranium X, parts with two α-particles, *i.e.*, with two atoms of helium; and lastly, that the atomic weight of helium is 3·994 (Watson); it follows that the difference in atomic weight between uranium and radium should equal $3·994 \times 3 = 11·98$. This condition also involves the assumption that no considerable number, or rather weight, of β-particles escapes. Taking the atomic weight of uranium as 238·5, and subtracting 11·98, the figure 226·52 for the atomic weight of radium follows. On the other hand, assuming that Richards and Merigold[*] have given the only trustworthy series of determinations of the atomic weight of uranium, the mean of their two series is 238·41. Zimmermann's work, giving an atomic weight of 239·62,[†] may be disregarded; also that of Aloy, which is unfavourably criticised by F. W. Clarke. Now, subtracting 11·98 from 238·41, 226·43 appears to be the calculated atomic weight of radium, corresponding well with our figure, 226·36.

The radium series is supposed to terminate in lead, with evolution of five α-particles; and the atomic weight of lead is given in the official table of atomic weights as 207·1. But we should expect $226·4 - 19·92 = 206·48$ for the atomic weight of lead. Clarke's general mean is 206·97; and, taking Baxter and Wilson's determinations, made in Richards' laboratory,[‡] the figure is 207·08. The difference is no less than 0·6 of a unit. This is inexplicable on the assumptions made above. One of the following conclusions must therefore be drawn:—

(*a*) That lead is not the final disintegration product of radium. But there is no known element of atomic weight 206·5, and no place for it in the periodic table.

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[*] 'Amer. Acad. Proc.,' 1902, vol. 37, p. 365.

[†] 'Ann. Chem.,' 1886, pp. 232, 299.

[‡] 'Amer. Acad. Proc.,' 1907, vol. 43, p. 365.

(*b*) That the atomic weights of radium and uranium are about 0·5 unit too low; this is not impossible, granting that the value 226·4, found by us, is only a minimum.

(*c*) That helium is not the only gaseous product of disintegration; such a possibility, if true, would, of course, render the calculation useless.

In the present state of our knowledge, redeterminations of the atomic weights of uranium and lead, especially of the former, would seem to be imperative. But, so far as the present state of our knowledge goes, it may be taken that the atomic weight of lead is probably fairly exactly known, and may be accepted as not far from 207. Adding to this 20, we have 227, a number considerably greater than that found for radium by us. But it must be remembered that our figure is to be regarded as a minimum one, because all likely impurities would lower the atomic weight.

Appendix.

It appears to us advisable to add some details dealing with the precautions taken in such work with the micro-balance, and also to reproduce some details illustrating the method.

The transformation of chloride into bromide and *vice versâ*, which served for the determination of atomic weight, has been described in outline in the earlier part of this paper. The process itself needs no special mention, but in the course of the researches it was found that certain precautions were essential when dealing with milligrammes and fractions of a milligramme, which were altogether unnecessary when working with larger quantities of material.

In weighing the bromide in the small silica bucket, the greatest care had to be taken to exclude moisture, although with large quantities in a silica crucible, no special precautions were necessary. Again, in transferring the bucket containing the radium bromide from the heating crucible to the desiccator, varying quantities of moisture were absorbed, and the weights of the same sample after successive heatings often differed considerably. It was found essential to displace the hygroscopic hydrogen bromide by some inert gas before transference; and hydrogen was first tried. To our surprise we found that the salt, when heated in this gas, gradually lost weight, although no alteration in its appearance was observed. The use of pure nitrogen for this purpose proved quite satisfactory; and even when the radium salts were heated in it to bright redness for over an hour, no appreciable change in weight could be detected.

The procedure finally adopted both for chloride and bromide was to displace the halogen hydride from the heating crucible by pure nitrogen, to heat the salt for about five minutes in this gas, and to transfer the bucket and its contents, while still hot, to the desiccator. After it was cold, the transference to the balance was effected as quickly as possible, and the case was immediately pumped out. Owing to the presence of barium oxide in the balance-case, it acted as a vacuum desiccator, and moisture was completely excluded during the weighings.

Although it had been found that the weight of a silica crucible containing a radium salt remained perfectly constant within the limits of sensibility of an assay balance after prolonged exposure to hydrogen chloride or bromide at bright redness, careful experiments were made to see if any alteration whatever occurred when the bucket, after the same treatment, was weighed on the micro-balance. At first it appeared as if the bucket increased slightly in weight, but it was found that the gain was only apparent, and was caused in all probability by the deposition of fine particles of dust on the balance-beam, in spite of the careful filtering of the air entering the case. The zero of the balance, though as a rule perfectly constant, was found to be liable to change, after the case had been filled or emptied more rapidly than usual. The counterpoise-bulb, and the weights suspended from the same arm of the balance as the bucket, had a much greater surface than their silica counterweight, and the deposition of dust-particles had thus the effect of increasing the apparent weight of any object weighed. With care in emptying and filling the case, this effect was negligibly small, but, in order to guard against the possibility of error, a silica tare, of nearly the same weight as the bucket, was constructed, and the pressure and temperature when the tare was balanced were always noted before carrying out a weighing. In this way, any shift in the zero-point of the balance between the weighings could be detected and allowed for. Subsequent experiments demonstrated the almost perfect constancy of weight of the silica bucket during the operations of an experiment.

The possible introduction of impurities into the salt during its conversion to chloride or bromide was carefully considered, but, on account of the gaseous nature of the substances effecting the transformation, possible sources of contamination were greatly restricted. The hydrogen chloride was evolved from pure "contact" sulphuric acid and solid ammonium chloride, and, after its passage through a tube filled with glass-wool, was led into the reaction-crucible. The nitrogen, prepared in the usual way, by leading a mixture of air and ammonia over red-hot copper, was stored in a large gas-holder over weak acid, and, before use, was passed again over red-hot copper, to eliminate the last traces of oxygen. It was dried by passage over concentrated sulphuric acid, and, finally, led through a tube packed with lumps of fused caustic soda. The hydrogen bromide, prepared as described at the beginning of this paper, was made from hydrogen evolved by the electrolysis of caustic baryta and very pure bromine. Calcium chloride was used to dry the hydrogen before its passage through the bromine, and the hydrogen bromide was freed from any traces of moisture by passage over anhydrous calcium bromide. The best proof, however, that the radium salt did not take up any impurities from the gaseous reagents lies in the fact that it was found possible, after converting the bromide to chloride, to reconvert the salt to bromide, and to recover the original weight almost exactly.

In carrying out a determination, the salt was always weighed after several successive treatings, until its weight ceased to change appreciably. Starting with the crystallised bromide, the salt was heated to redness in hydrogen bromide in the manner described, transferred to the balance, and its weight was determined approximately. It was then re-heated for half an hour, and an accurate weighing was made. This process was repeated until the weight became constant. The conversion to chloride was usually complete after a two hours' heating, and, after this, weighing to constant weight was carried out as before. Re-conversion to bromide required about four or five hours' heating. The weighings themselves were rather tedious, as it was found to be imperative to leave the balance for an hour, so as to allow of the establishment of complete temperature equilibrium before the readings were made.

We append a full calculation of the results of the weighings of sample 6.

	Zero reading.	Pressure corr. to 0°.	Temp.	Weight of air displaced by bulb.
Silica tare on balance	259	435·4	° 19·0	235·4 × 0·0784 /292·0 = 0·10945
Bucket on balance......	258	424·0	18·5	424·0 × 0·0784 /291·8 = 0·10666
Bucket and bromide (final weight)	257	108·6	18·3	108·6 × 0·0784 /291·3 = 0·02787
Bucket and chloride (final weight)	261	378·8	18·6	378·8 × 0·0784 /291·6 = 0·09536
Silica tare	257	435·8	19·0	435·8 × 0·0784 /292·0 = 0·10955

Weight of bromide:—

Weights used to balance bromide	2·51198 mgrm.
Weight added by bulb	−0·07929 „
Zero correction	+0·00001 „
Vacuum correction = 0·000342 mgrm. per atmosphere per milligramme = 108/760 × 2·43 × 0·000342..................	+0·00011 „
	2·43281 „

Weight of chloride (since the tare has not altered appreciably in weight, the same weight for the empty bucket was taken):—

Weights removed to balance chloride	1·88379 mgrm.
Weight added by counterpoise-bulb, 0·10666 − 0·09536......	−0·01130 „
Zero correction, 3 × 0·000014	−0·00004 „
Vacuum correction, 379/760 × 1·87 × 0·000306	+0·00031 „
True weight of chloride	1·87276 „

Hence, change of weight on conversion, 2·43281 − 1·87276 = 0·56005 mgrm. The atomic weight is given by the equation, where 159·84 = Br_2, and 70·92 = Cl_2,

$$x + 0·56006 = 1·87276 \times 159·84 - 2·43281 \times 70·92;$$

whence $$x = 226·35.$$

Details of the other experiments are set forth in the table appended. Finally, in case the radium results might have been affected by some constant error, the atomic weight of barium was determined in exactly the same manner as that of radium. Merck's guaranteed pure barium chloride, containing only a trace of alkalies, was recrystallised four times from pure distilled water. The salt was then precipitated by means of gaseous hydrogen chloride, recrystallised once more from pure water in a silica vessel, and a specimen taken for analysis. The results obtained were:—

	Weights added.	Air displaced.	Zero correction.	Vacuum correction.	True weight.	Atomic weight.
Barium bromide	3·52843	−0·02299	−0·00032	+0·00045	3·50557	137·37
„ chloride	2·51198	−0·05535	−0·00011	+0·00016	2·45668	137·32
„ bromide	3·52843	−0·02309	+0·00004	+0·00045	3·50583	

The International table for 1911 gives, for barium, the atomic weight 137·37; and these values are sufficiently close to prove that the method is free from any constant error.

Table.

		Weights removed.	Weights applied by pressure change.	Zero correction.	Vacuum correction.	True weight.	Weight difference. $RdBr_2-RdCl_2$.	Atomic weight.
		mgrm.				mgrm.		
Samples 1, 2 and 3 ...	Bromide	2·93802	−0·02401	+0·00014	+0·00043	2·91458	0·67314	225·2
	Chloride	2·24686	−0·00589	+0·00011	+0·00036	2·24144		
„ 1, 2 and 3 ...	Bromide	2·93802	−0·02401	+0·00001	+0·00043	2·91415	0·67302	225·19
	Chloride	2·24686	−0·00617	+0·00008	+0·00035	2·24118		
Sample 3	Bromide	1·47944	+0·02201	0	+0·00028	1·50117	0·34640	225·48
	Chloride	1·13833	+0·01638	−0·00021	+0·00018	1·15474		
„ 4	Bromide	0·44846	−0·07936	0	0	0·36910	0·08510	225·9
	Chloride	0·34109	−0·05738	+0·00028	+0·00001	0·28400		
„ 6	Bromide	2·92863	−0·07616	+0·00003	+0·00012	2·85262	0·65676	226·40
	Chloride	2·22246	−0·02685	0	+0·00025	2·19586		
„ 6	Bromide	2·83065	−0·06985	−0·00015	+0·00019	2·76084	0·63592	226·25
	Chloride	2·12692	−0·00249	+0·00014	+0·00035	2·12492		
„ 6	Bromide	2·61935	−0·00868	−0·00014	+0·00046	2·61099	0·60110	226·35
	Chloride	2·01955	−0·01003	+0·00003	+0·00033	2·00988		
„ 6	Bromide	2·51198	−0·07929	+0·00001	+0·00011	2·43281	0·56006	226·35
	Chloride	1·88379	−0·01130	−0·00004	+0·00031	1·87275		
„ 7	Bromide	2·37622	−0·01579	−0·00019	+0·00038	2·36062	0·54351	226·45
	Chloride	1·88379	−0·06676	−0·00004	+0·00012	1·81711		

An Optical Determination of the Variation of Stress in a Thin Rectangular Plate Subjected to Shear.

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(Communicated by Prof. Karl Pearson, F.R.S. Received December 28, 1911,—Read February 8, 1912.)

Introduction.—The determination of the distribution of shear stress in a body subjected to the action of an arbitrary set of forces applied to its bounding surfaces is often of great importance in constructional work. In most cases mathematical difficulties do not allow of an exact solution, while the simplifying assumptions which are often made to reduce these difficulties lead to formulæ which are probably not correct even to a first approximation. It is important, therefore, to have experimental determinations to compare with the values calculated by approximate methods to determine to what extent the assumptions are correct, and also, if possible, to afford data for better approximations in cases which do not allow of mathematically exact solutions.

The shear stresses in riveted joints, the stiffened webs of plate girders and such like structures, afford examples of practical problems of extreme complexity from the mathematical standpoint, which are dealt with in practice by rough approximations, using large factors of safety fixed by experience of the behaviour of similar structures, in order to allow for contingencies due to ignorance of the actual stresses and accidental overloading. The experimental determination of the state of stress in a body as inferred by measurements of the strains produced at its surface affords a means, which has been used by various investigators, to determine the condition of stress in a body subjected to the action of forces applied at its boundary. In shear problems, with which the present paper deals, this usually involves the measurement of small angular displacements, but these strains are so minute for the materials of construction at ordinary working stresses that it is usually found necessary to make experiments on other materials like indiarubber, plasticine and the like, which afford strains sufficiently large for accurate measurement, while their elastic properties are such that they may be considered to behave like more intractable materials with fair accuracy.

Another possible method of attack is to use a material possessing optical properties which depend on the applied stresses, and by measuring the change in optical property to infer the stress in the material. For this purpose glass possesses very many advantages, in that its action on polarised light depends on the stress in the material and, to a first approximation, a linear law expresses the relation between the stress and the optical effect produced.

Glass can be obtained in a very perfectly elastic condition, and the stress strain relations resemble those of steel and wrought iron very closely. Unfortunately, measurements of the optical effects produced usually require stresses in the neighbourhood of fracture, and this, coupled with the difficulty of shaping the material into other than the simplest forms, has prevented its use becoming general for this kind of investigation.

At the present time other transparent bodies may be used which do not offer this kind of objection, and in the investigation to be described a commercial form of transparent nitro-cellulose is employed which has, in a high degree, most of the desirable properties of glass and few of its disadvantages.

If a beam of plane polarised light is passed through a plate of glass, or the like transparent material, it is found that the relative retardation R produced between the ordinary and extraordinary rays depends on the difference between the principal stresses $\widehat{rr}$ and $\widehat{\theta\theta}$, at any point (r, θ), and also on the thickness T of the material. We may express the relation by the formula

$$R = C(\widehat{rr} - \widehat{\theta\theta})T,$$

where C is a constant. This retardation is easily measurable, and the values of $(\widehat{rr} - \widehat{\theta\theta})$ may be inferred in a simple manner by a mechanical measurement to be described.

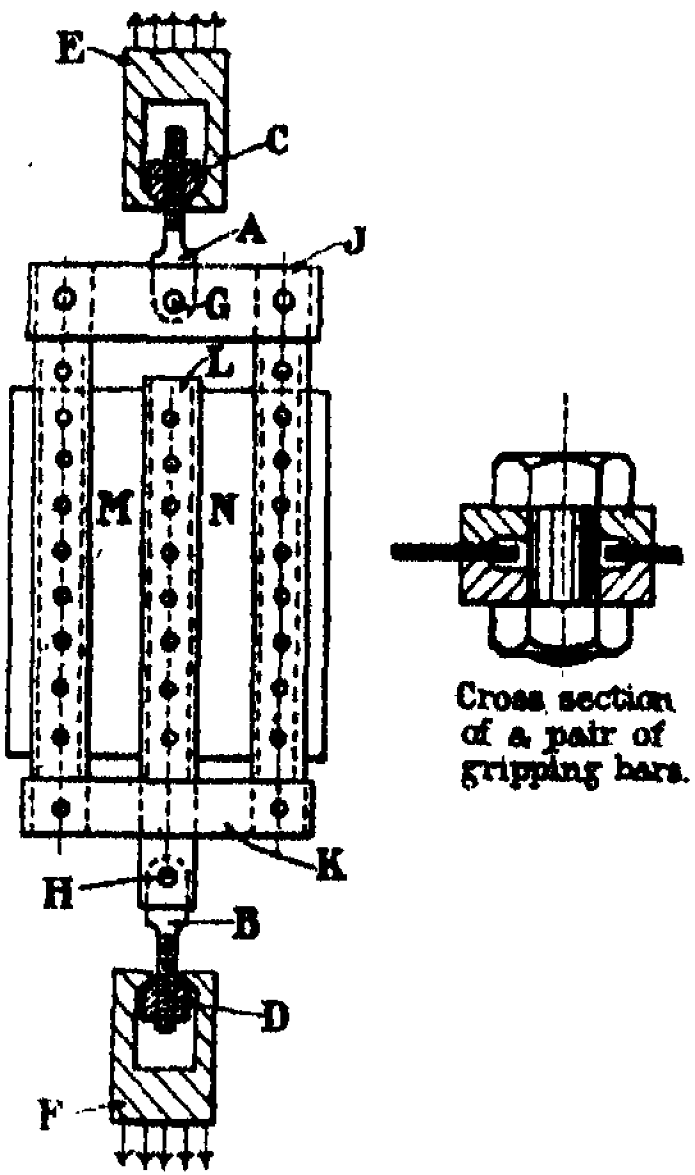
The distribution of the shear stress in the cross section of a dam has, of late years, been the subject of many experimental and theoretical investigations, and one of the outstanding difficulties of this problem is the unknown distribution of the shear stress in the horizontal sections of a dam.

At the suggestion of Prof. Karl Pearson some experiments were made, in the autumn of 1910, on the related and more simple problem of the distribution of shear stress in a rectangular plate, by an optical method then being used by the author in another investigation.

These earlier experiments on a small model gave promise of fairly accurate quantitative results with a large experimental apparatus, and, as a preliminary to the more difficult problem of the shear stress in a dam, an apparatus for experimental work was constructed on what appeared to be a sufficiently large scale, and it was set up in the engineering laboratory of the City and Guilds of London Technical College, Finsbury.

Description of the Apparatus and the Method of Experiment.—A small tension testing machine of the simple lever type was available for applying stress to a plate. It was capable of exerting a maximum pull of 6000 lbs., and it had a clear gap between the end shackles of 20 inches. In order to adapt the machine for the purpose of applying shear stresses a steel frame was constructed to give a symmetrical double shear to a plate of the transparent material. The arrangement adopted is shown in the accompanying sketch (fig. 1), in which A, B, are eye-bolts provided with nuts C, D, having spherical ends fitting into the shackles E, F, of the testing machine. When these latter are separated by the action of the machine the line of pull passes through the centres of the pins G, H, to which the frame proper is secured. This frame consists of pairs of vertical planished steel bars of 2 inches by 9/16 inch rectangular cross-section, the outer pairs being pin-connected above to a pair of cross-bars J, 3 inches by 5/8 inch in cross-section, and below to a similar but lighter set K.

Each gripping bar is slightly undercut for the greater part of its width, leaving narrow faces on each side, so that when the plate to be stressed is placed in position and the bolts adjusted in the holes provided, the bars grip the plate along its whole length on each side. The extent of the gripping surfaces is indicated by dotted lines in fig. 1 and by the accompanying cross-section. The central bars L are constructed in the same manner, and when a pull is applied by the testing machine the free parts M, N, of the plate are subjected to a nearly pure shear. The maximum length of plate which can be accommodated in the apparatus is 14 inches, and horizontal cross-bars are provided to permit free widths of $\frac{1}{2}$ inch, 1 inch, and 2 inches respectively.



Cross section of a pair of gripping bars.

FIG. 1.

The general arrangements of the testing machine and frame are shown in fig. 2, in which a simple lever A pivoted at B supports the stressing frame on a spherical bearing R, and the lower shackle R_1 engages with a similar bearing. The load is applied by a wire C attached to a spring balance D hanging from the outer end of the lever. The wire passes over a pulley E to a frame F provided with a nut G threaded on a screw H, which latter is turned by a hand-wheel J.

This arrangement has some advantages over an alternative method employed at an early stage of using dead weights at the outer end of the testing machine lever. This necessitated the lifting and frequent changing of masses of as much as 150 lbs. weight in some experiments, thereby involving much labour and waste of time. The same load can be applied with ease by a few turns of the hand-wheel and changed for a new load in a few seconds without shock or jar. It is, however, open to the objection that a spring balance is hardly ever quite accurate, and that its indications vary slightly from time to time owing to changes in temperature and the like. These objections are to a great extent removed by careful calibrations, and these were carried out at intervals and the observations corrected therefrom. The differences proved to be very small, and were practically almost negligible. At the commencement of an experiment the machine was balanced by adjusting the position of the weight J on the screw K, and a load was put on the specimen by turning the hand-wheel until the spring balance registered a definite pull. The distances between the knife-edges on the main lever were such that the pull on the specimen was 20 times the pull shown on the balance, while the weight of the central pair of bars and shackles always added a load of 15 lbs. to the plate under shear, of which due account was taken.

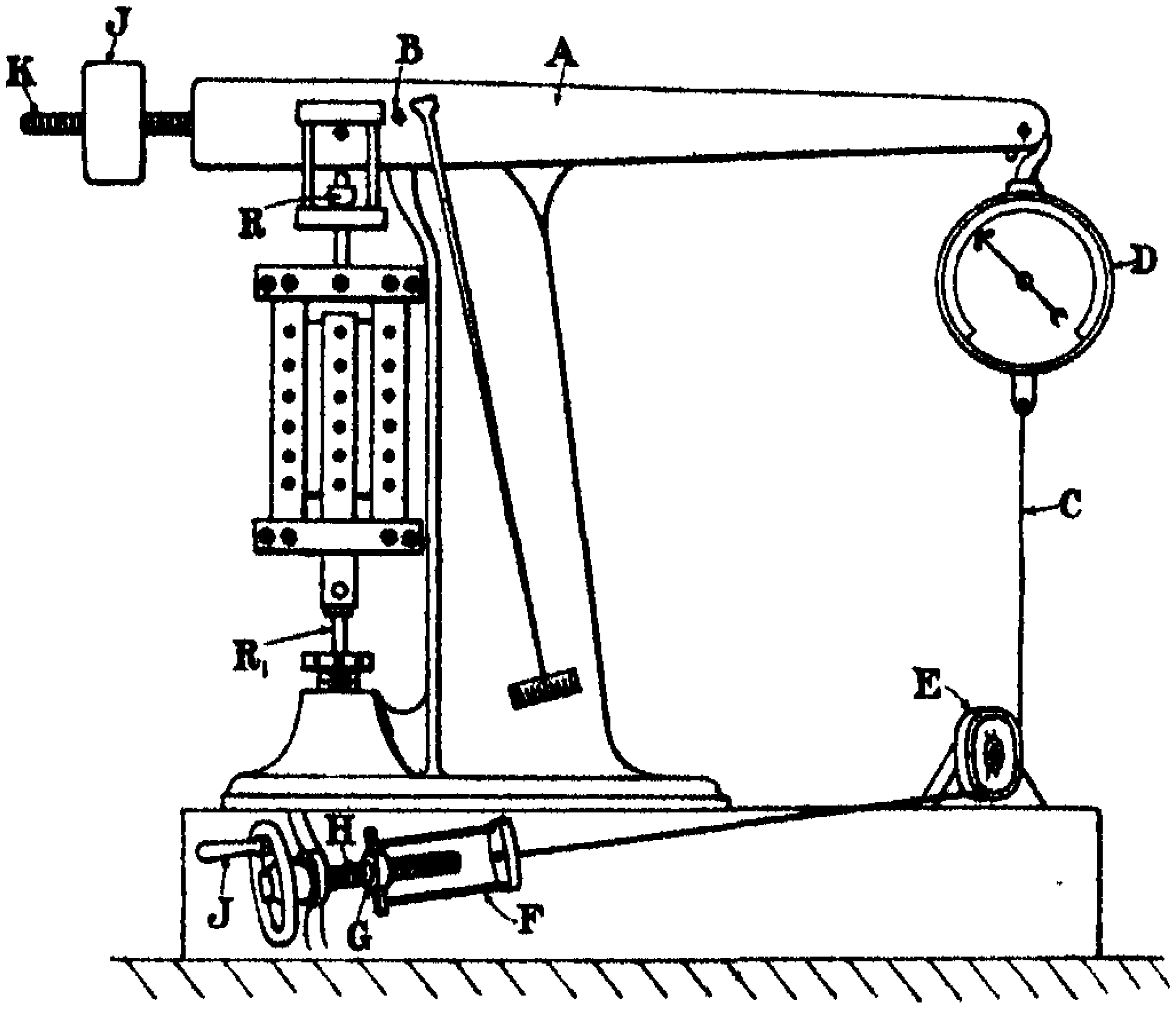


Fig. 2.

Arrangement of the Optical Apparatus.—In the earlier experiments this consisted of a pair of Nicol prisms and suitable focussing lenses for producing a parallel beam of light from an arc lamp. The field of view with such an arrangement was very small, and with the apparatus available the maximum area under observation at any one time was practically a circle of about 1½ inches diameter.

To examine the optical effects produced over a long length of plate the apparatus was supported on an optical bench and carried by a rising and falling table, which latter could be adjusted by screws to bring any part of the plate under observation.

This caused much waste of time due to the frequent changes of position required and the numerous minor adjustments of the optical apparatus. The arrangement was ultimately replaced by a much more convenient apparatus designed for me by Prof. Silvanus Thompson, F.R.S., which enabled a plate 10 inches in length to be examined in detail without any change in the adjustments of the optical apparatus except an alteration in height of the Nicol prism used as an eyepiece. This new apparatus consisted of a black glass plate 24 inches by 12 inches, set at a suitable angle for polarising the light obtained from a number of glow glamps, and diffused through tissue paper screens. Quarter wave plates of mica were also constructed about one square foot in area for obtaining circularly polarised light. This apparatus was set up in the neighbourhood of the stressed plate, and the colours due to double refraction were observed by the aid of a Nicol prism, which when set at close range enabled any point to be examined in detail, while the whole plate could be viewed from a distant position at one time.

The positions of any stress maxima or minima could therefore be approximately determined from the colours by a qualitative examination, and any stress variations due to imperfect adjustments could be localised.

For quantitative work it is most convenient to determine the stress produced by reference to a colour scale, and this may be either a calibrating member stressed in the same way as the plate under experiment until the colour effects are identical, or an optical wedge might be arranged to give a graduated retardation of any fraction of a wave-length of light to correspond to that given by the stressed plate. In the present experiments, however, the most obvious method was to take advantage of the fact that a pure shear is equivalent to a pair of equal strains at right angles and equally inclined to the direction of slide, one a stretch and the other a squeeze. If a tension member cut from the same plate is stressed in the direction of the compression stress the retardation produced by the one is annulled by the other for a definite pull on the calibration member.

Let the tension member be subjected to a stress T, then the strain s_1 in the direction of its length is given by $T = Es_1$, where E is Young's modulus; the lateral contraction s_2 produced in the breadth of the member is $s_2 = -\eta s_1$, where η is the stretch-squeeze ratio.

These strains are equivalent to a slide σ and an all round stretch x at a point, and we may express the relations between them by

$$s_1 = \tfrac{1}{2}\sigma + x, \qquad s_2 = -\tfrac{1}{2}\sigma + x,$$

from which we obtain

$$x = \tfrac{1}{2}s_1(1-\eta) \quad \text{and} \quad \sigma = s_1(1+\eta).$$

Now, since the shear stress $S = \mu\sigma$, where μ is the coefficient of rigidity of the material, we obtain

$$S = \mu s_1(1+\eta) = \tfrac{1}{2}Es_1 \quad \text{or} \quad S = \tfrac{1}{2}T.$$

The shear at any point may therefore be determined from the stress in a tension member set along the direction of compression and stressed to give total extinction at the point considered.

The tension stress in the calibration member also produces a change in the thickness c of the material of an amount expressed by $-\eta s_1 c$.

Experiments* have shown that the value of Young's modulus for this material is approximately 300,000, measured in pounds and inches, and that η is 0·39. The change in thickness per 1000 lbs. of stress intensity is therefore $-0·0013\,c$. The highest stress recorded in any experiment is 4730 lbs. per square inch, corresponding to a diminution of rather less than 0·0062 of the thickness of the material. In the majority of the experiments the stress rarely exceeded 2000 lbs. per square inch, and the joint correction for the calibration member and the shear specimen is therefore so small that it is well within the limits of error of the determinations, and no corrections have been applied.

It is necessary to determine the directions of the principal stresses at points in the plate where measurements are to be taken, and these can be mapped with considerable accuracy if the plate is examined by aid of a pair of Nicol prisms, with their principal planes at right angles. At any point where the directions of principal stress correspond to the principal planes of the crossed Nicol prisms no light can pass to the eye, and all points in the field of view for which this condition obtains are mapped by a black band or black area, which, in general, alters in position when the prisms are rotated.

An examination of the stressed plate shows that the directions of principal stress are inclined at 45° to the line of pull of the frame except at the ends, where the directions change somewhat rapidly. The observed changes in angular position for one end of a plate having a length of 4 inches and a breadth of 1 inch are shown in fig. 3, from which it will be observed that for the centre line all these variations occur within ⅛ inch from the edge. Hence, if measurements are made along the centre line of this plate the tension member must be set at an angle of 45° to the line of pull for all positions not very close to the ends. This is also evident from a map of the lines of principal stress obtained from the curves of observation, and shown by fig. 4.

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* 'Phil. Mag.,' October, 1910.

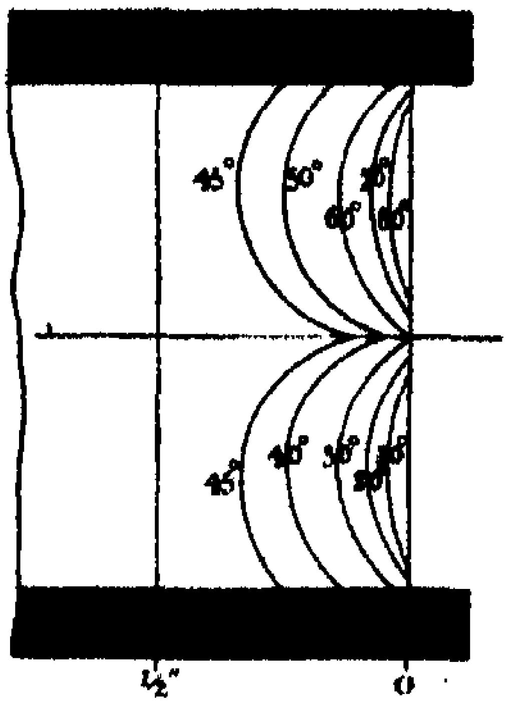

Fig. 3.

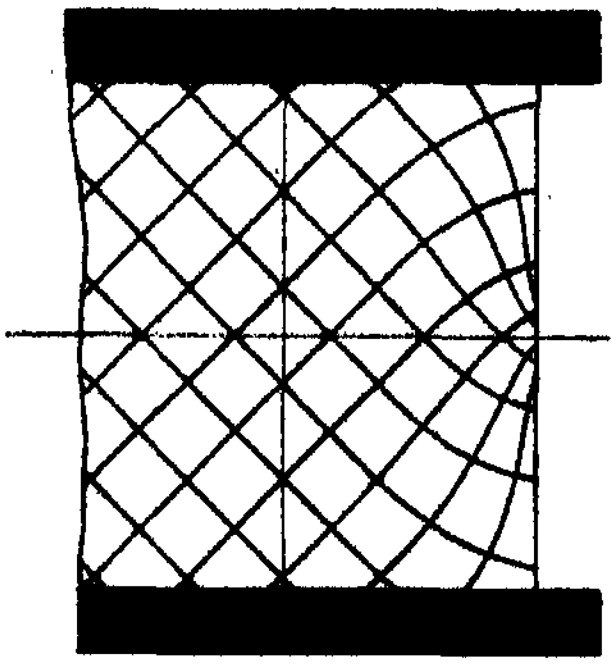

Fig. 4.

The breadth of the plate influences the distribution at the ends, and the disturbing effect upon the positions of the lines of principal stress appears to be approximately proportional to the breadth, as appears from fig. 5, which shows the lines of equal inclination corresponding to a plate

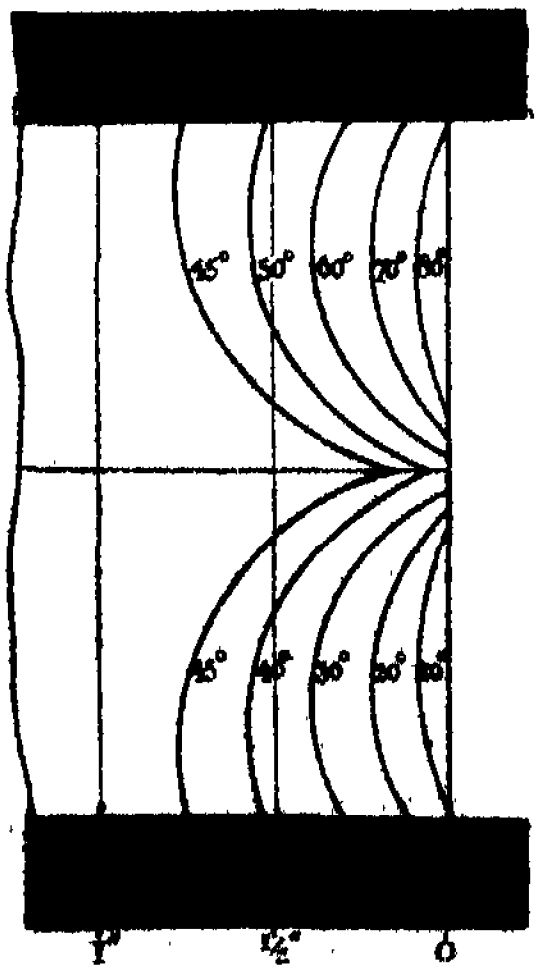

Fig. 5.

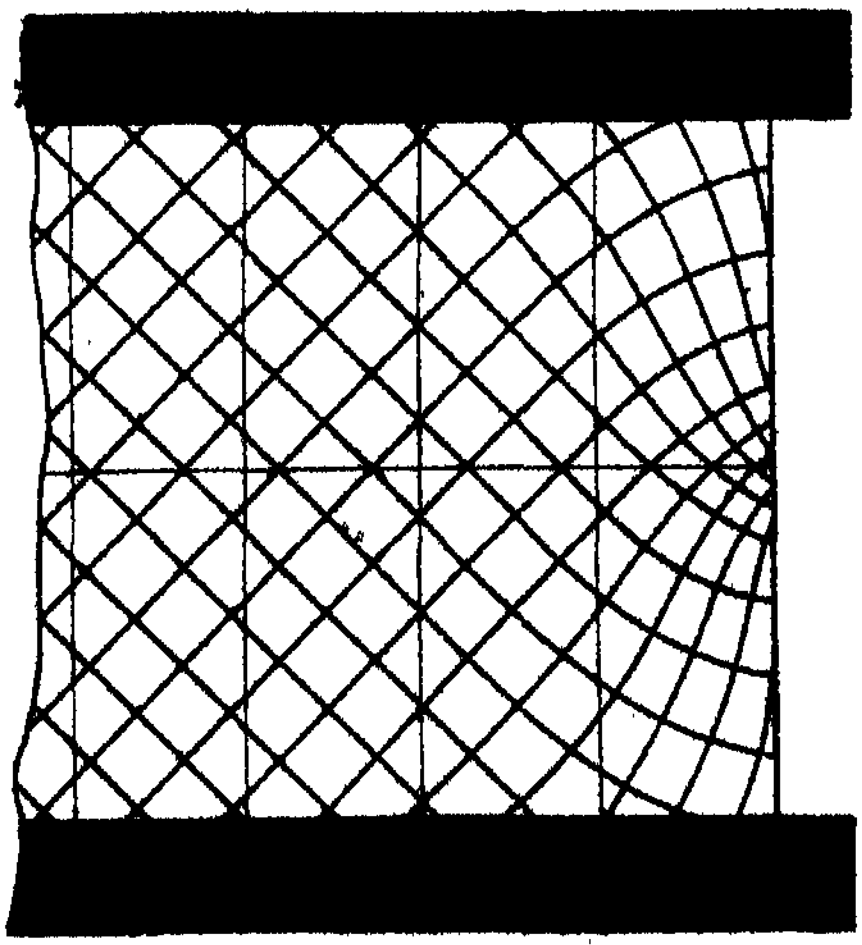

Fig. 6.

2 inches in breadth and 4 inches in length. For this breadth, measurements of the shear stress were taken along the central line, and also along lines parallel thereto, and ½ inch away from the sides. The lines of principal stress and equal inclination at one end of this plate are shown in fig. 6, from which it appears that along the central line no correction is required unless the distance is less than ¼ inch from one end, while along a line parallel and ½ inch away from the central line a correction will be required for this width of plate if the distance is less than ¾ inch from one end.

For applying load to a calibrating member set along the direction of compression stress in the plate a miniature lever testing machine was constructed (fig. 7), so that the specimen could be adjusted in angular position.

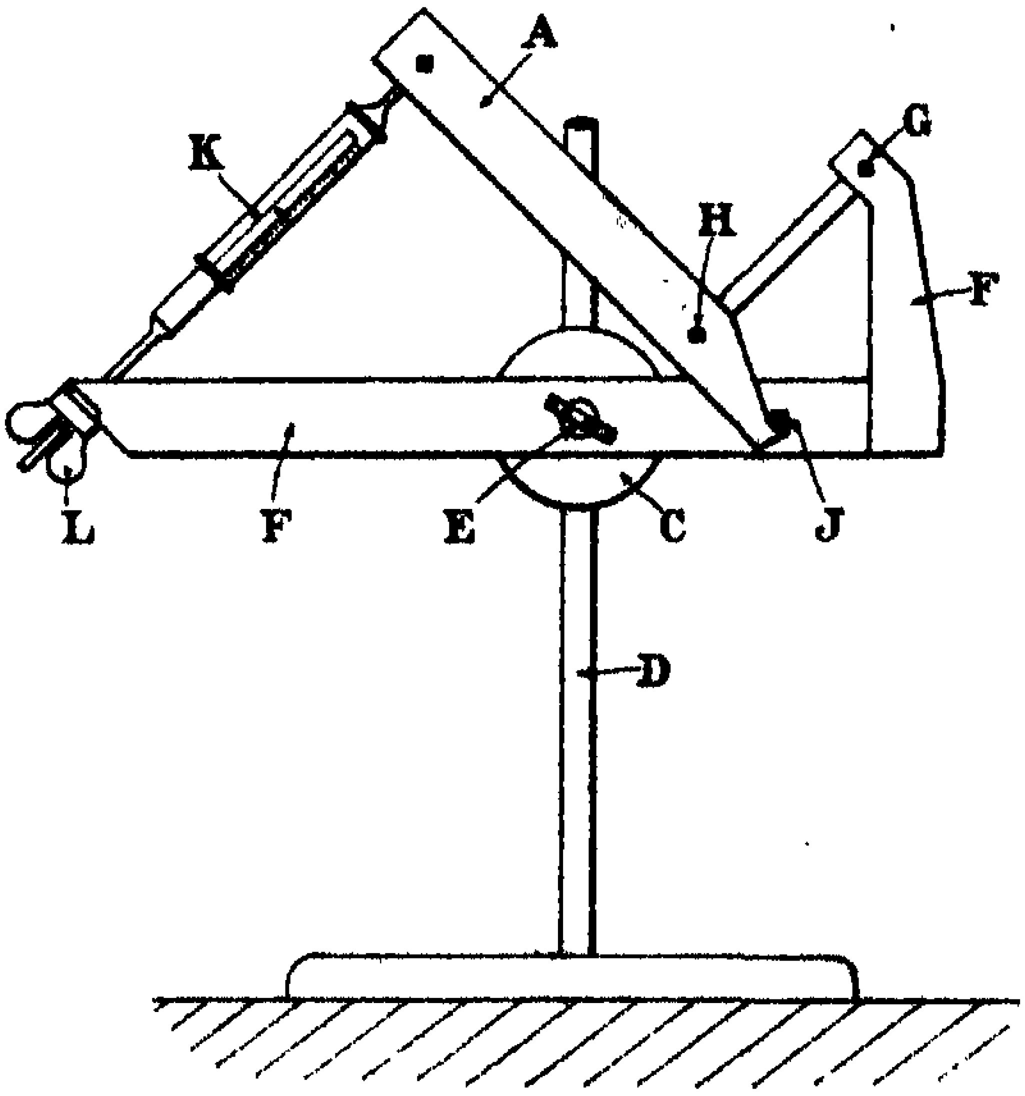

FIG. 7.

This consists of a right-angled frame F, supported on a swivel pin E, carried by a block C, which latter slides on a vertical rod D. Clamping screws are provided to fix the block in any position along the vertical rod and to adjust the angular position of the frame. One end of the specimen is carried by a knife-edge G, and the other by a similar knife-edge H, in a lever A, which latter is pivoted about a knife-edge J, secured in the frame. A pull on the specimen is obtained by a spring balance K, one end of which is attached to the outer end of the main lever, and the other passes through a hole in the frame, and is secured by an adjusting nut L for regulating the pull.

In order to obtain a uniform tension stress in the specimen each end is drilled, and steel rings are inserted in the holes so made to receive the knife-edges, which latter pass through the rings, and are supported on each side of the specimen by cheek plates.

The weight of the inclined lever and spring balance produces a total pull on the specimen of 2·8 lbs., and the lever multiplies the pull of the balance by five, so that if the dimensions of the cross-section of the calibration member are determined the stress on the material can be calculated. In all cases the calibration specimen was cut from a part in close proximity to the plate used as the specimen under shear stress.

Method of Experiment.—A plate of material, of approximately the required size, was first cut from the sheet, and examined for flaws between crossed Nicol prisms. If it proved satisfactory, the plate was afterwards drilled for clamping in the frame, and finished to the required size. It was then covered with a network of reference squares by marking with a fine needle point, and, before setting in place, it was again examined, to make sure that the shaping processes had caused no injury to the material. With the specimen clamped in position, the maximum load was applied, and a further optical examination was made, to discover if there were any signs of local stresses due to unequal tightening of the bolts, or due to direct pressure of a bolt on the circumference of the holes. This examination was easily carried out by observing the appearance of the plate from a considerable distance by aid of a Nicol prism set to give total extinction at no load. If the colours indicated local stresses, the gripping forces of the bolts were adjusted until these colours disappeared and similarly disposed colour effects were observed on both free widths under shear. The colour indications were very sensitive to the slight adjustments which were usually found necessary at the commencement of each experiment, and the application of stress by the gripping surfaces was probably very uniform, and a close approximation to an evenly distributed shear stress along the vertical sides.

The central arrangement of the applied loads, and the construction of the stressing frame, ensured that both lengths of the plate were loaded in exactly the same manner. The gripping surfaces were maintained at the same distance apart by large turned bolts, fitting exactly into holes in the cross-bars—these holes were reamered to ensure an accurate fit, and were probably true to one thousandth of an inch. During the experiments, no tilt of the frame was observed which would tend to make the outside vertical members approach one another, and, as a large tilt would be required to cause a very small horizontal displacement, it was assumed that the arrangement of the frame effectually held the bars at the correct distance apart at all loads. This is an important matter, because a central load applied to the frame produces shear in the material, and, if the outer plates are free to approach each other, an unbalanced bending moment is produced. If, however, as in the present instance, the tendency to bend is resisted by the frame, we obtain a practically pure shearing stress in the material. In earlier experiments, the same result was obtained on a single plate A, fig. 8,

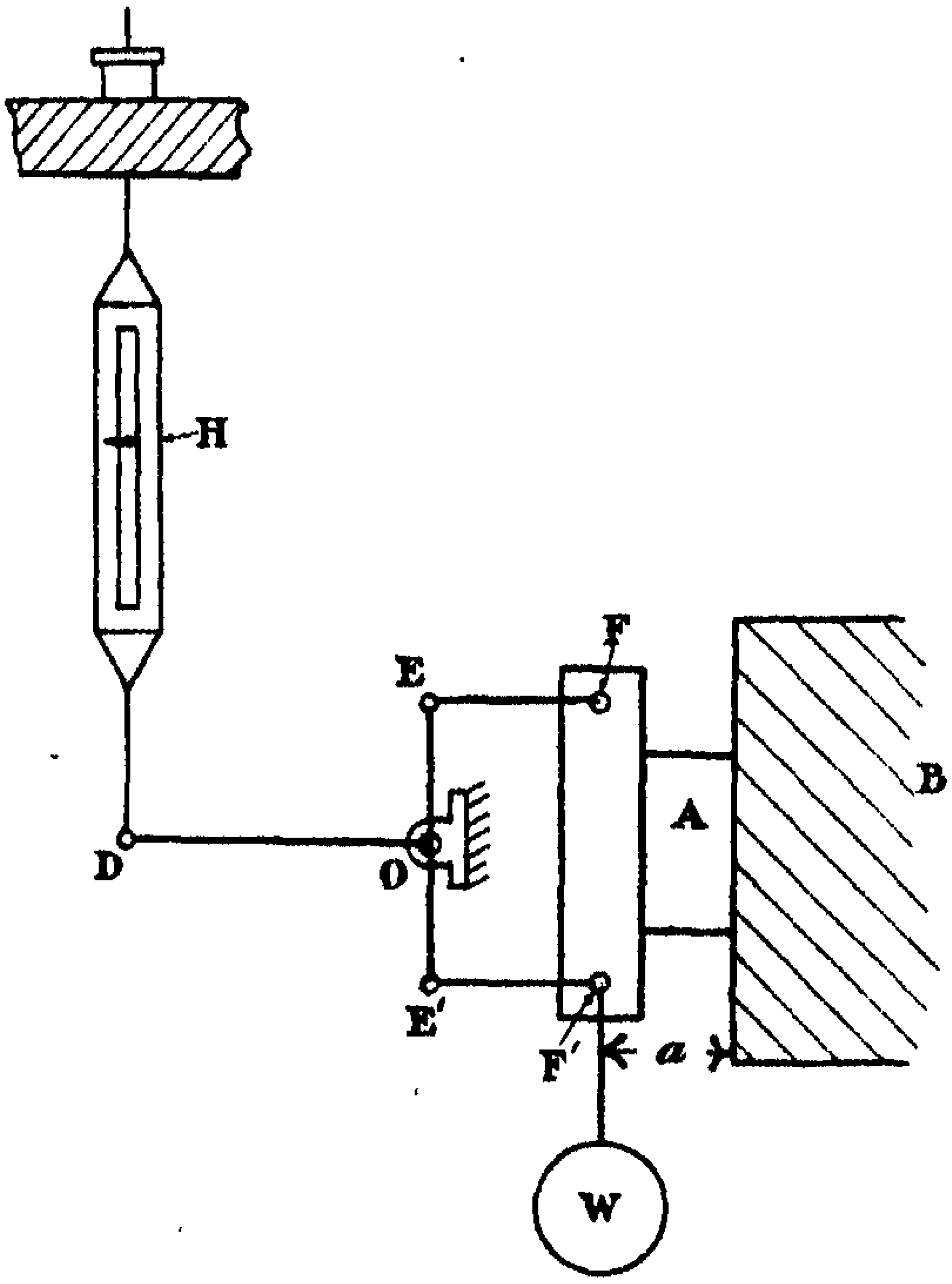

FIG. 8.

held rigidly in a support B, and loaded by a weight W, by supplying an opposing couple of amount W*a*. This was accomplished by using a double bell-crank lever EOE'D, pivoted at O, and connected to the outer gripping plates G by equal links EF, E'F'. A pull at D was furnished by a spring balance H, which was adjusted to give a moment of the required amount about the fixed centre O.

Observations of material in both frames gave similar indications, while the effect of an unbalanced bending moment could also be observed in this arrangement. A point-to-point examination of the stress distribution was made by aid of the calibration member, which was adjusted to any required height, with its line of direction at an angle of 45° to the frame. The stress in this tension member was first adjusted until the colour effect at the place under observation was extinguished and a dark field obtained. The mean value obtained by first slightly passing the stress at which extinction was observed, and then afterwards lowering the stress until this position was again passed, was taken as the measure of the shear stress in the plate under observation.

Analytical Theory.—The mathematical theory of the distribution of stress due to shear in a rectangular section may be considered with reference to the case of a cantilever joist, fig. 9, loaded by a weight W at its outer end, the term joist denoting that the length l is many times the depth h, and that the thickness b is small compared with the depth. At any cross section distant x from the origin there is a couple $W(l-x)$ and a shear W, both of which are balanced by the stresses $\widehat{xx}$ and $\widehat{xy}$ set up in the interior of the beam. The couple can be balanced if the stresses $\widehat{xx} = -12W(l-x)y/bh^3$, where y is the distance from the central plane, while the stress $\widehat{xy}$ must satisfy the general equations of equilibrium,

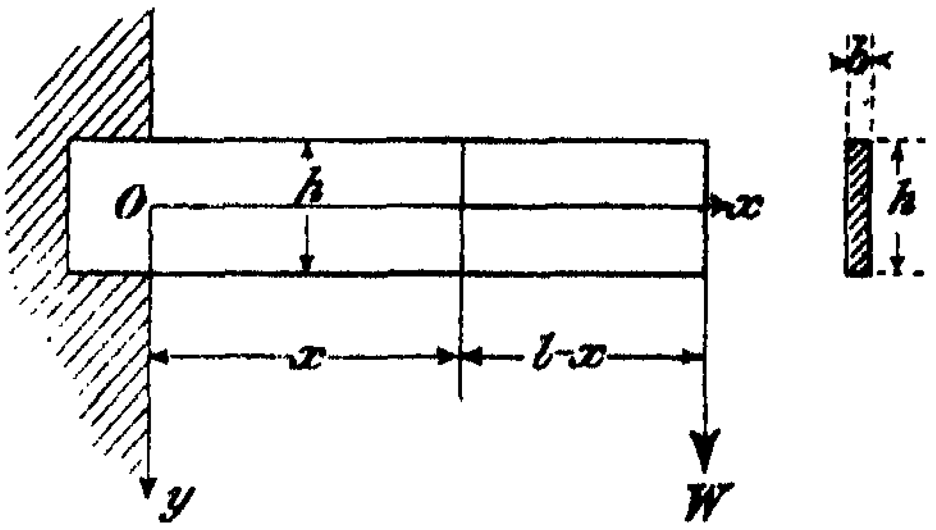

FIG. 9.

$$\frac{\partial \widehat{xx}}{\partial x} + \frac{\partial \widehat{xy}}{dy} = 0, \quad \text{and} \quad \frac{\partial \widehat{xy}}{\partial x} = 0,$$

the stresses being taken as averages throughout the thickness of the plate.

In addition, the sum of the shear stresses taken over the vertical section must have the same total magnitude as the shear load W, and the value of $\widehat{xy}$ must be zero at the upper and lower surfaces of the beam. These conditions are fulfilled if

$$\widehat{xy} = \frac{3}{2}\frac{W}{bh}\left(1-\frac{4y^2}{h^2}\right),^*$$

provided that the terminal load W is distributed over the end section according to this parabolic law. In general the accurate distribution of the load over the terminal section is of no importance in practical applications to beams, since they are usually of considerable length compared with their depth, but it has often been assumed that the shear stress in any rectangular section is distributed according to this parabolic law, even in such extreme cases as that of the section of a reservoir wall or a dam, where the conditions of the application of the load and the dimensions of the section are widely different from those assumed in the simple theory.

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* Love, 'Mathematical Theory of Elasticity,' p. 137.

In the case of a plate of rectangular section subjected to uniformly applied shear stresses over the longer edges, there appears to be no good reason for the assumption that the shear distribution follows a parabolic law, unless the width of the plate is comparable with the depth. If the plate is very long compared with its width, and the distribution is uniformly applied over the vertical edges, it would also appear from general considerations that the shear stress must be very uniform over a considerable length. For if we imagine the vertical shear stresses equilibrated by shear stresses of the same intensity applied along the two horizontal ends, the condition of the plate becomes one of uniform shear throughout, and it seems improbable, if these latter applied forces be removed, that any considerable variation in shear stress can be caused thereby except near the ends. Andrade[*] has considered the case of a rectangular block of length $2a$ and breadth $2b$ with the upper and lower faces subjected to uniform shifts in their own planes in opposite directions, all the remaining faces being free, and he obtains for the distribution of shear stress $\widehat{xy}$ the form

$$\widehat{xy} = \Sigma \mathrm{A}\mu \sinh 2na\,(x/a\,.\sinh nx - \tanh na \cosh nx) \cos ny,$$

where A and n are complex and the summation is for all values of n, where $\sinh 2na = 2na$; and x is the distance from the central plane of the block. This gives large maximum values near the ends and some maxima and minima of much less importance distributed along the central length.

Experimental Results.—The general method of experiment having been described, we now turn to the values obtained. One of the early experiments with the shear apparatus above was made on a plate which had a thickness of 1/16 inch and a free width of 1 inch. A length of 10 inches was chosen as the most convenient maximum, as all the experiments could then be made without altering the adjustments of the polarising apparatus. The plate was subjected to a pull of 100 lbs. per inch run, and calibrations of the testing machine showed that 99 lbs. per inch run was actually applied, the remaining 1 per cent. being accounted for by errors in the balance and frictional resistance of knife-edges. The weight of the middle bars of the frame was also added to the above load in this set of experiments.

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[*] "The Distribution of Slide in a Right Six Face subject to Pure Shear," 'Roy. Soc. Proc.,' A, vol. 85, 1911.

Commencing with the maximum length the plate was subjected to a total load of 997·5 lbs. on each side, corresponding to an average shear stress of 1595 lbs. per square inch, and the central section was explored from end to end by the calibration member. The stresses in the tension member which caused total extinction at any given point are shown in Table I for

Table I.

Position measured from top.	Stress in calibration member (lbs. per square inch).				
	Load on shear plate (lbs.).				
	997.	600.	304.	205.	106.
inches.					
0	0	0	0	0	0
$\frac{1}{8}$	—	—	—	1405	1760
$\frac{1}{4}$	1945	2130	2210	2565	3660
$\frac{3}{8}$	—	—	—	3450	4460
$\frac{1}{2}$	3155	3170	3220	3840	4780
$\frac{5}{8}$	—	—	—	—	4520
$\frac{3}{4}$	—	3240	3510	4110	3920
$\frac{7}{8}$	—	—	—	—	2075
1	3290	3250	3460	4210	0
$1\frac{1}{4}$	—	—	—	4110	
$1\frac{1}{2}$	3200	3285	3440	3770	
$1\frac{3}{4}$	—	—	—	2630	
2	3200	3235	3500	0	
$2\frac{1}{4}$	—	—	3480		
$2\frac{1}{2}$	3190	3210	3200		
$2\frac{3}{4}$	—	—	2240		
3	3150	3195	0		
$3\frac{1}{2}$	—	3210			
4	3110	3210			
$4\frac{1}{2}$	3125	3225			
5	3125	3250			
$5\frac{1}{4}$	—	3150			
$5\frac{1}{2}$	3125	2550			
$5\frac{3}{4}$	—	1610			
6	3125	0			
$6\frac{1}{2}$	3125				
7	3130				
$7\frac{1}{2}$	3135				
8	3170				
$8\frac{1}{2}$	3200				
9	3230				
$9\frac{1}{4}$	3170				
$9\frac{1}{2}$	2690				
$9\frac{3}{4}$	1730				
10	0				

intervals of 0·5 inch, except at the ends, where more frequent observations were taken. These values are also shown in a more convenient way by fig. 10, in which the observed stresses are plotted as abscissæ against the lengths measured from one edge as ordinates. The shear stress at any point in the central line of the plate has a numerical value of one-half that of the tension stress plotted in this and succeeding figures.

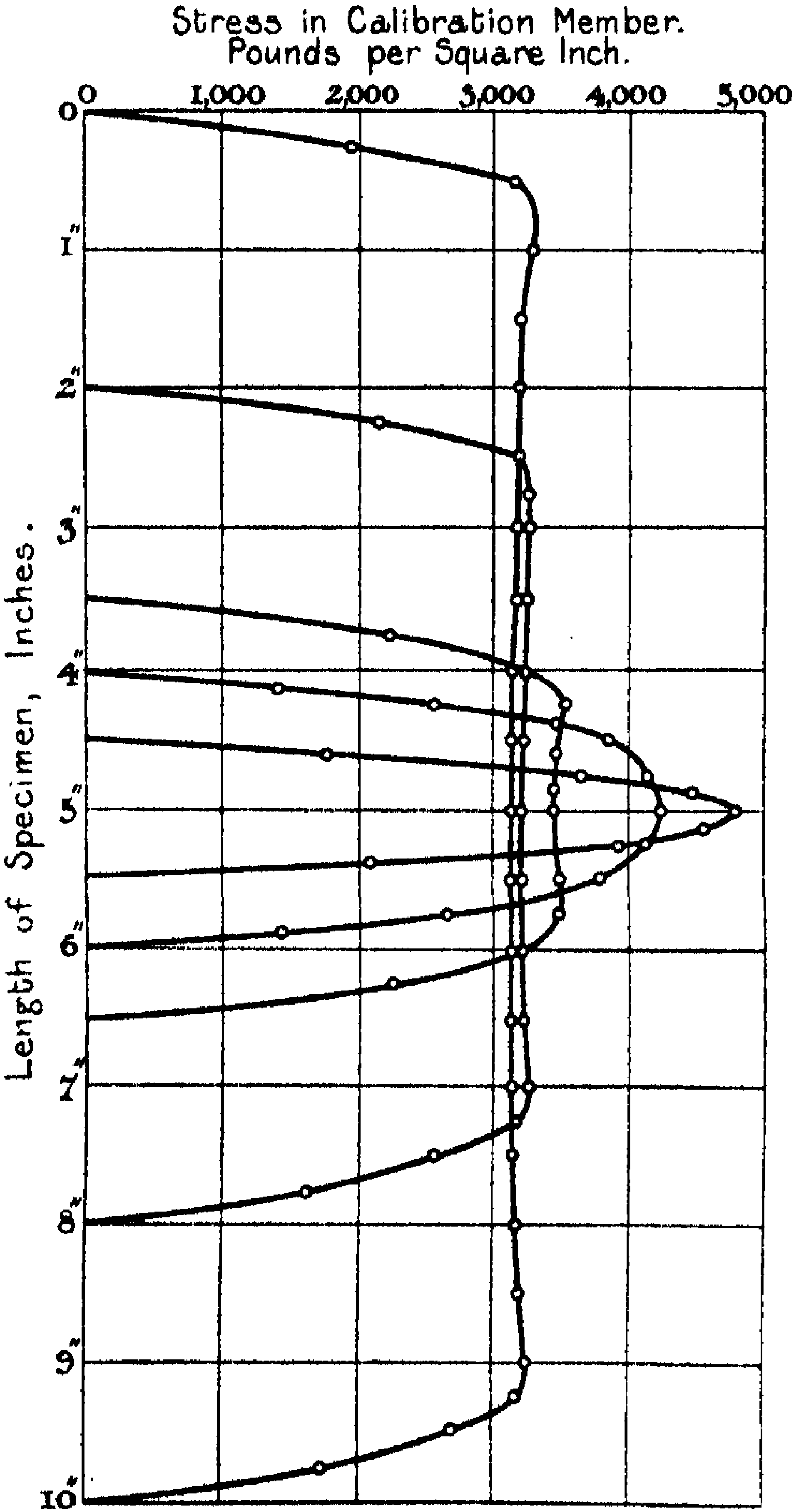

FIG. 10.

It will be observed that the distribution has certain important characteristics. Starting from, say, the upper edge, it rises very rapidly from a zero value until, at a distance of rather less than the width of the plate, it reaches a maximum value. From this point there is a slight decline in the stress intensity until in the neighbourhood of the centre of the plate a minimum value is reached; and, as we proceed in the same direction, there is a gradual recovery to a maximum value at a distance from the lower edge of the plate which corresponds very well with the position of the upper maximum, the stress finally falling to zero at the lower edge.

The general accuracy of the experimental work may be tested by a determination of the mean value of the tension stress from a summation of the area of this diagram. If this value is compared with the mean intensity of the applied shear we ought to find that this latter is one-half the numerical value of the tensional stress, provided we may assume that the optical effect has a linear relation to both tension and shear. In the present example this ratio was found to be 1·89.

In order to discover the effect of an alteration in the ratio of length to breadth, the same plate was cut to a length of 6 inches by removing equal portions from each end. The applied load was maintained at nearly the same mean intensity, and readings similar to those of the previous experiment were obtained, as shown in the annexed table. A slight increase of the shear stress was observable over the middle portion of the length, with maxima spaced nearly as before. The ratio of tension to shear in this case was found to be 1·87. In the same manner a length of 3 inches was also examined, which gave more pronounced maxima, nearly symmetrically spaced; the ratio of the stresses was 1·88.

The shear distribution in the 2-inch length, however, underwent a change, it no longer had a double maximum, but increased in value from the edge to the centre. The principal result of this change in the distribution was to raise the maximum stress by a considerable amount, as the diagram shows, and a still further reduction in length to 1 inch gave a similar distribution curve which approximated to a parabolic form with a further increase of stress intensity.

These experiments show fairly well the general features of the distribution, which are characterised by a fairly uniform distribution of stress over the greater part of a long length, rising slightly to a maximum near the ends and falling rapidly to zero at the edges. As the length diminishes the maximum values approach one another, until they finally merge into a maximum value at the centre for some ratio of length to breadth, which the experiments show to be in the neighbourhood of two.

A measure of the accuracy of the values contained in Table I is afforded by the accompanying Table II, from which it will be observed that the percentage differences between the experimental and calculated values range between 2·5 and 6·5 per cent., and they indicate that the measured tension stresses are in defect, a result which may be due to inaccuracies in the observations or imperfections in the material, or both. These percentage differences are given for each set of experimental values.

Table II.

Length of specimen.	Mean applied shear stress.	Measured tension stress.	Tension stress ÷ shear stress.	Percentage difference from the theoretical value.
inches.	lbs./sq. in.	lbs./sq. in.		
10	1595	3020	1·89	−5·5
6	1600	2990	1·87	−6·5
3	1625	3020	1·88	−6·0
2	1645	3250	1·95	−2·5
1	1700	3250	1·91	−4·5

Experiments were also made on a similar plate ½ inch in free width and having a length of 8 inches. The loads imposed were slightly different from those of the previous case, owing to the dead weight of the middle bars being allowed for in the application of the load, which latter was maintained at a uniform amount of 100 lbs. per inch run of plate, corresponding to a mean stress of 1584 lbs. per square inch on the specimen when due account is taken of friction and other errors. The curves of equal inclination showed that the principal stresses were equally inclined to the central line for distances up to within 1/16 inch from the ends. This plate yielded results which agree very well with those described above as shown by Table III and the accompanying fig. 11. Commencing with the full length, we have the same characteristic distribution as in the former case, and this is repeated with a length of 4 inches, except that the intermediate stress is slightly less than before. Further reductions in the length of the specimen to 2 inches and 1½ inches respectively show somewhat similar stress distributions with maxima closer together and a general increase in numerical magnitude, while for a length of 1 inch we obtain a single central maximum value corresponding to a stress intensity in the calibration member of 4150 lbs. per square inch. The final length of ½ inch, for which the plate assumes a square form, also gives a very symmetrical shear curve with a very large increase in the stress. It is interesting to compare the stresses at the centre of this length with that on the 8-inch length under the same mean loads per unit of length. The former gives a shear stress of 2335 lbs. per square inch as compared with 1725 lbs. per square inch on the longer length or an increase of 36 per cent. in the intensity of the stress.

Table III.

Position measured from top.	Stress in calibration member (lbs. per square inch).					
inches.						
0	0	0	0	0	0	0
1/16	—	—	—	—	—	1600
1/8	—	2300	1990	2370	2620	3000
3/16	—	—	—	—	—	4150
1/4	2110	3390	3260	3650	3650	4670
5/16	—	—	—	—	—	4150
3/8	—	—	—	—	3900	3000
7/16	—	—	—	—	—	1600
1/2	3400	3580	3720	4020	4150	0
5/8	—	—	—	—	3900	
3/4	—	3500	3590	3970	3650	
7/8	—	—	—	—	2600	
1	3500	3890	3550	4020	0	
1 1/4	—	—	3620	3520		
1 3/8	—	—	—	2370		
1 1/2	3460	3380	3660	0		
1 3/4	—	—	3260			
1 7/8	—	—	2180			
2	3460	3330	0			
2 1/2	3450	3350				
3	3450	3360				
3 1/4	—	3460				
3 1/2	3450	3580				
3 3/4	—	3330				
4	3450	0				
4 1/2	3440					
5	3430					
5 1/2	3440					
6	3450					
6 1/2	3460					
7	3480					
7 1/2	3180					
7 3/4	1780					
8	0					

In considering the question of the experimental accuracy which may be regarded as possible, it seems probable, using a material like xylonite which is not perfectly elastic, that there will be deviations from linearity of both the elastic and the optical properties of the material, and so far as these considerations affect the experiments we may expect more accurate results with a lower stress.

The mechanical measurements of the loads imposed by the spring balances and the ratios of the lever arms of the testing machinery can be determined very accurately in most cases, and the calibrations which were made render it extremely probable that errors from this source are very

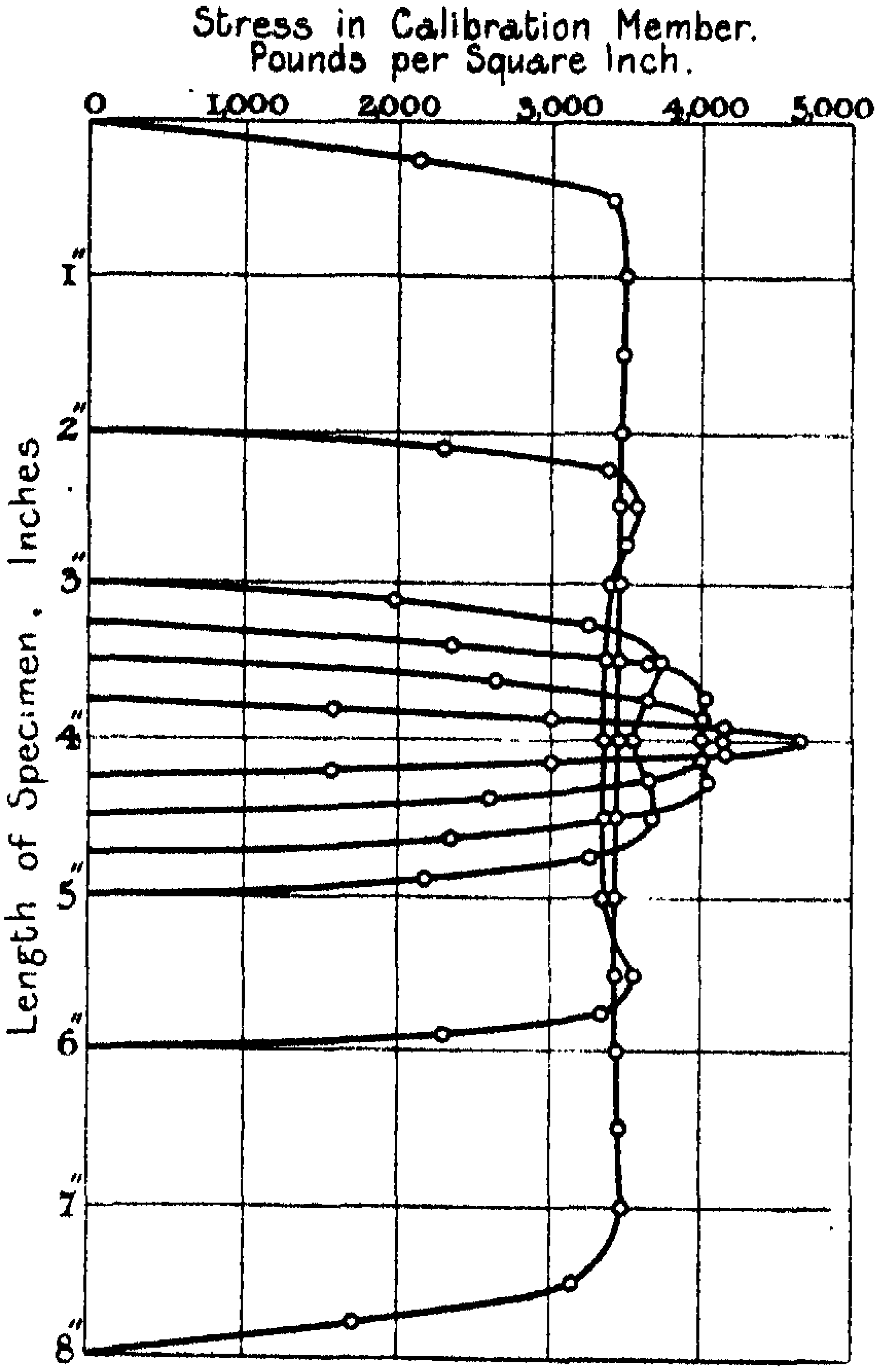

FIG. 11.

slight except at small loads. The estimation of the stress at which total extinction takes place is more difficult, especially at low stress intensities, but experience shows that readings can be made with considerable accuracy.

The errors due to defective elasticity and want of linearity in the relation between stress and optical property probably account for the major portion of the differences between the experimental and calculated ratios of the tension stress to the shear stress. As will be seen from the accompanying Table IV, these differences are sufficiently small to allow the general distribution of shear to be made out with considerable accuracy.

An attempt was made to carry out experiments on a plate of this thickness, 2 inches wide and 10 inches deep. The material, however, buckled under the load, and the lateral distortions produced optical effects which made measurements of shear impossible.

Table IV.

Length of specimen.	Applied stress.	Mean value of measured tension stress.	Tension stress ÷ shear stress.	Percentage difference from the theoretical value.
inches.	lbs./sq. in.	lbs./sq. in.		
8	1584	3125	1·970	−1·50
4	1584	3250	2·050	+2·50
2	1584	3240	2·045	+2·25
1½	1584	3270	2·064	+3·20
1	1584	3250	2·050	+2·50
½	1584	3100	1·957	−2·20

As the foregoing experiments at a high working stress could not be completed owing to the buckling of the thin plate, it was considered advisable to study the stress distribution at low loads, and a sheet of transparent material was therefore obtained of the greatest thickness procurable, 0·186 inch, and from this three plates were cut and ruled, as described above. They were each 10 inches in length and of ½ inch, 1 inch, and 2 inches width respectively. The applied load was in all cases proportional to the length of the plate, and for convenience it was fixed at 15 lbs. on the spring balance reading per inch length of plate. Allowing for an error in defect of 1 per cent., as already mentioned, this amounted to an actual load of 148·5 lbs. per inch run.

The procedure was much the same as in the earlier experiments, but the experience of former work showed, among other details, that it was of primary importance to have all the bolts very accurately adjusted to give equal intensities of grip on the plate to avoid local stresses and consequent error of measurement. Although the applied stress was much lower than before, the increased thickness of plate multiplied the optical effect so considerably that no difficulty was experienced in making the required measurements.

The plate of ½ inch width, when under test, showed all the principal features brought out by previous experiments. The numerical values obtained are shown in the accompanying Table V, and these values are plotted in fig. 12.

Table V.

Position measured from top.	Stress on calibration member (lbs. per square inch).			Position measured from top.	Stress in calibration member (lbs. per square inch).			
inches.				inches.				
0	0	0	0	0	0	0	0	0
⅛	—	—	1260	$\frac{1}{16}$	—	—	—	930
¼	725	1660	1675	⅛	1220	1205	1170	1555
½	1240	1825	1835	$\frac{3}{16}$	—	—	—	1960
¾	1515	1760	1750	¼	1700	1745	1850	2215
1	1662	1675	1700	$\frac{5}{16}$	—	—	—	1960
1½	1705	1670	1665	⅜	1825	1925	1960	1545
2	1700	1670	1605	$\frac{7}{16}$	—	—	—	970
2½	1690	1635	1590	½	1835	1810	1995	0
3	1690	1645	1630					
3¼	—	—	1710	⅝	—	—	1940	
3½	1690	1620	1795	¾	1825	1715	1830	
3¾	—	—	1665	⅞	—	—	1184	
3⅞	—	—	1205	1	1740	1795	0	
4	1690	1680	0					
				1⅛	—	1870		
4½	1686	1640		1¼	1767	1790		
5	1685	1700		1⅜	—	1220		
5¼	—	1700		1½	1790	0		
5½	1685	1745						
5¾	—	1590		1¾	1750			
6	1700	0		1⅞	1220			
				2	0			
6½	1715							
7	1715							
7½	1690							
8	1690							
8½	1760							
9	1685							
9¼	—							
9½	1160							
9¾	785							
10	0							

An inspection of these curves shows that the maxima become very pronounced as the depth diminishes, and that at a ratio of depth to span of two approximately the central maximum asserts itself and continues to do so for any further reduction in length.

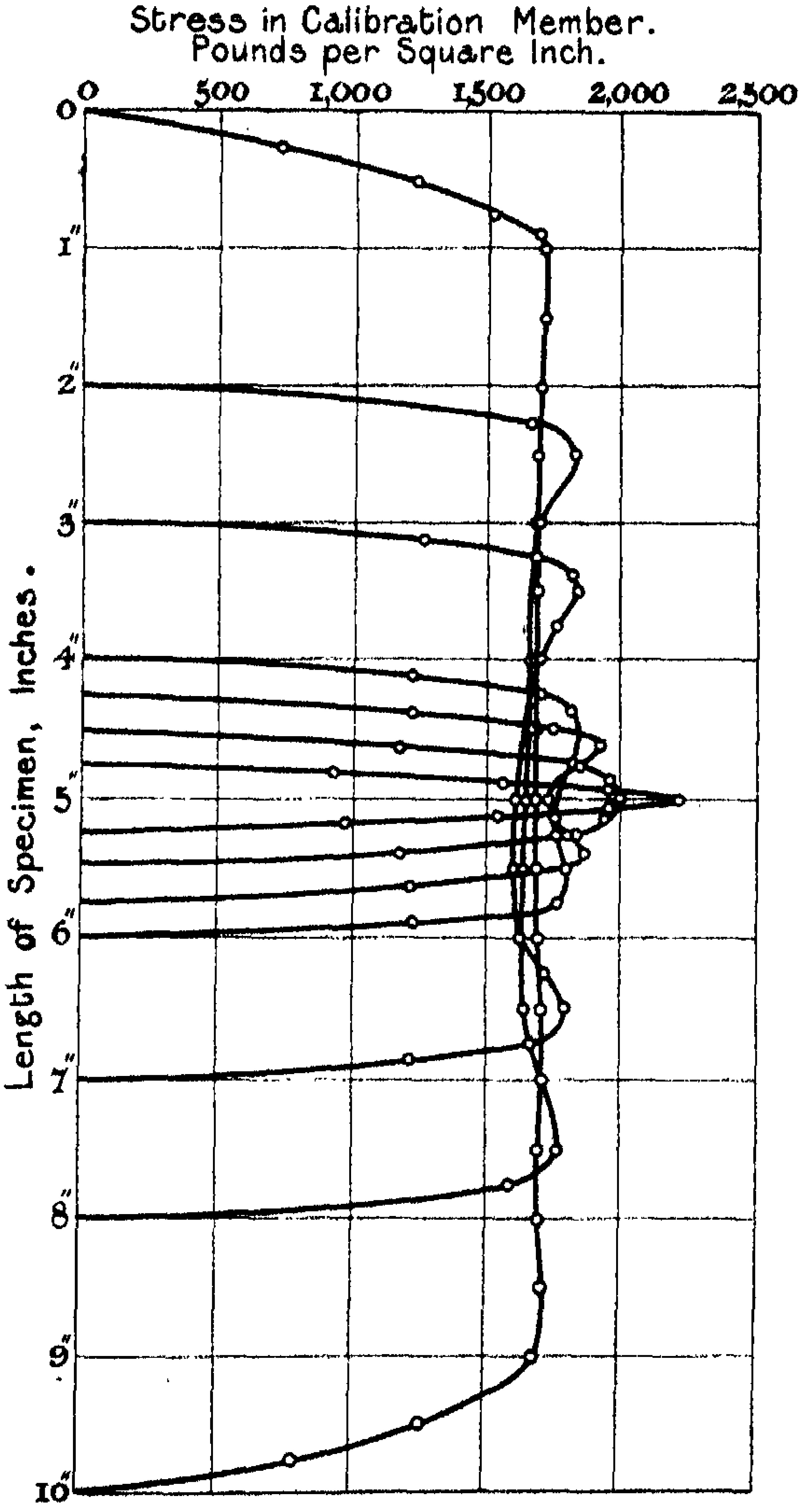

FIG. 12.

A comparison of the mean tension stress required to produce extinction with the mean shear stress actually applied is shown in Table VI, and the percentage difference column indicates that the shear distribution curves account very completely for the applied stress with the exception of the last experiment, which is in considerable defect; this is probably due to the uncertainty of the value of the small load applied to the specimen in a testing machine of so large a capacity. It is interesting to note that nearly all the maxima and minima are very pronounced, and that the former occur at distances from the extreme edges nearly equal to the width of the plate.

Table VI.

Length of specimen.	Applied shear stress.	Measured tension stress.	Tension stress ÷ shear stress.	Percentage difference from the theoretical value.
inches.	lbs./sq. in.	lbs./sq. in.		
10	798	1575	1·97	−1·5
6	798	1638	2·05	+2·5
4	798	1612	2·02	+1·0
2	798	1652	2·06	+3·0
1½	798	1590	1·99	−0·5
1	798	1530	1·92	−4·0
½	798	1500	1·86	−7·0

The 10-inch length shows a want of agreement with the remaining experiments in this respect. This is probably due to a slight want of uniformity in the application of the shearing force at the ends of the full length of plate, as it occurred in other similar cases, while in shorter lengths the

Table VII.

Position measured from top.	Stress in calibration member (lbs. per square inch).			Position measured from top.	Stress in calibration member (lbs. per square inch).			
inches.				inches.				
0	0	0	0	0	0	0	0	0
¼	740	1075	1140	⅛	670	625	720	1035
½	1265	1580	1605	¼	1110	1255	1370	1750
¾	1590	1810	1870	⅜	1440	1555	1740	2150
1	1705	1770	1825	½	1700	1780	1920	2310
1½	1705	1715	1750	⅝	—	1958	2140	2180
2	1705	1690	1705	¾	1910	2075	2195	1795
2½	1700	1685	1720	⅞	1885	2040	2130	1075
3	1695	1670	1780	1	1860	2010	1920	0
3¼	—	—	1835					
3½	1685	1675	1590	1⅛	—	2015	1705	
3¾	—	—	1095	1¼	—	2055	1405	
4	1680	1690	0	1⅜	—	1995	780	
				1½	1795	1830	0	
4½	1670	1705						
5	1660	1795		1⅝	—	1590		
5¼	—	1825		1¾	—	1255		
5½	1660	1665		1⅞	—	655		
5¾	—	1070		2	1880	0		
6	1675	0						
				2⅛	1890			
6½	1680			2¼	1885			
7	1685			2⅜	—			
7½	1685			2½	1675			
8	1700			2⅝	1405			
8½	1715			2¾	1110			
9	1720			2⅞	690			
9¼	1625			3	0			
9½	1330							
9¾	815							
10	0							

agreement is a close one. The minimum values of the shear stress are not always at the centre, as may be observed from the distribution curves for the 6-inch, 4-inch, and 1½-inch lengths; these distortions are very slight, and might easily be accounted for by a slight want of uniformity in the application of the shear load.

Experiments on a plate of 1-inch width gave somewhat similar results, but of greater uniformity; the numerical values obtained are given in Table VII, and these values are plotted in fig. 13. The maximum values are, in general, reached at a distance of about ¾ inch from the ends of the

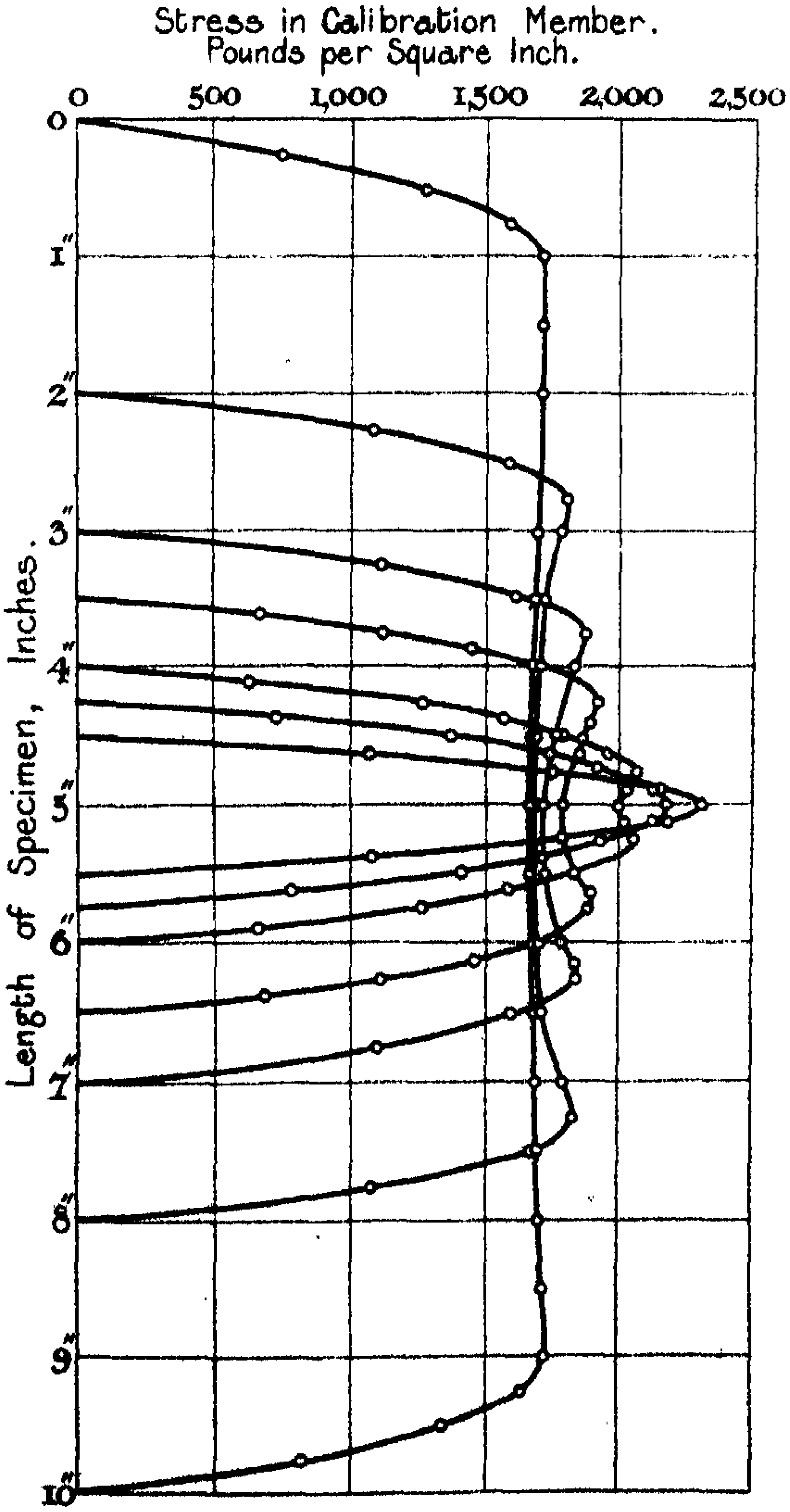

FIG. 13.

plate in all cases except that of the full length. The change to the form with a maximum at the centre is not complete for a length of 2 inches but becomes so for a length of 1½ inches, a result which agrees with the positions of the other maxima in all but the full length, but is not in good agreement with other determinations. The minimum values are very clearly defined, and are practically at the centre in every case where they occur. This set of experiments shows a much closer approach to the theoretical standard, as will be observed by the results collected in Table VIII, from which it appears that the percentage differences are with one exception all very small and negative.

Table VIII.

Length of specimen.	Applied shear stress.	Measured tension stress.	Tension stress ÷ shear stress.	Percentage difference from the theoretical value.
inches.	lbs./sq. in.	lbs./sq. in.		
10	798	1580	1·975	−1·25
6	798	1602	2·004	+0·20
4	798	1580	1·975	−1·25
3	798	1580	1·975	−1·25
2	798	1570	1·965	−1·75
1½	798	1574	1·970	−1·50
1	798	1580	1·980	−1·00

The experiments made on a plate of 2 inches width were directed to determine the stress distribution not only along the central section, but also at sections midway between this and the sides of the gripping bars.

The results obtained (Table IX) show that the distribution near the sides is very similar to that of the central section, for some distance remote from the ends, and in most cases the differences are within the limits of experimental error. At the ends, however, there are considerable changes (fig. 14), especially as the length of the specimen is diminished, and the change in the directions of the lines of principal stress becomes an increasingly important factor. Except close to the ends, however, the general features of the distribution are shown to remain unchanged; figs. 6 and 7 indicate that the observations on each side of the central line require correction for distances within ¾ inch from the ends. This slightly affects a few values at a distance of ½ inch from the ends, where the lines of principal stress are inclined at approximately 52° and 38° to the central line. Subsequent measurements on another specimen, when the calibration member was set in accordance with the angles indicated above, showed that these corrections amounted to approximately 4 per cent., and the curves of shear stress on

Table IX.

Position measured from top.	Stress in calibration member (lbs. per square inch).														
	Left.	Centre.	Right.	Left.	Centre.	Right.	Left.	Centre.	Right.	Left.	Centre.	Right.	Left.	Centre.	Right.
inches.															
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
¼	—	410	—	—	425	—	—	560	—	—	605	—	—	1000	—
½	940	850	—	1000	995	1030	1370	1210	1208	1295	1265	—	1750	1700	—
¾	1295	1170	1295	1360	1330	1425	1530	1455	1555	1704	1750	1870	2035	2120	2225
1	1480	1465	1495	1515	1570	1555	1740	1715	1710	2030	2030	2040	2330	2340	2370
1¼	—	—	—	—	—	—	—	—	—	—	—	—	2015	2115	2120
1½	1625	1625	1610	1750	1740	1750	1995	2005	2005	2220	2300	2220	—	1720	1725
1¾	—	—	—	—	—	—	—	—	—	—	—	—	—	1220	—
2	1690	1705	1700	1795	1795	1780	2005	2005	2005	2105	2045	1960	0	0	0
2¼	—	—	—	—	—	—	—	—	—	1855	1745	1680			
2½	1710	1705	1715	1795	1815	1780	2010	2005	2010	1440	1410	1385			
2¾	—	—	—	—	—	—	—	—	—	—	675	—			
3	1680	1685	1715	1805	1815	1790	1760	1770	1810	0	0	0			
3¼	—	—	—	—	—	—	1480	1480	1480						
3½	1700	1705	1705	1795	1795	1790	1130	1075	1220						
3¾	—	—	—	—	—	—	—	670	—						
4	1710	1710	1700	1795	1805	1795	0	0	0						
4½	1695	1685	1690	1820	1835	1810									
5	1700	1695	1695	1750	1745	1730									
5¼	—	—	—	1575	1560	1625									
5½	1700	1695	1695	1385	1295	1280									
5¾	—	—	—	—	630	—									
6	1700	1700	1705	0	0	0									
6½	1700	1705	1705												
7	1705	1715	1700												
7½	1700	1700	1700												
8	1695	1685	1625												
8½	1705	1670	1575												
9	1440	1425	1425												
9¼	1255	1205	1255												
9½	890	925	1200												
9¾	—	446	—												
10	0	0	0												

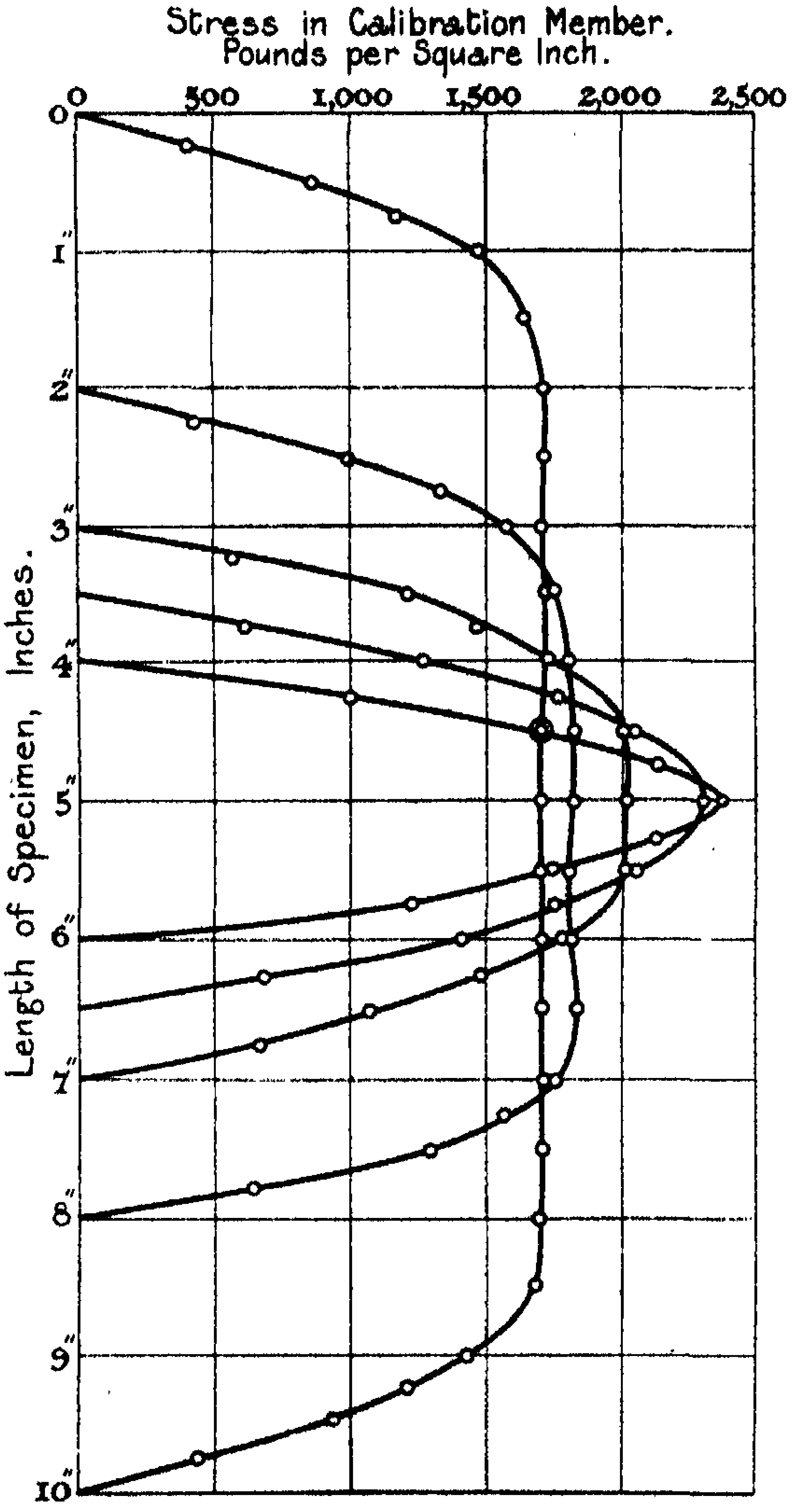

Fig. 14.

each side of the central line are slightly higher at the ends than the table indicates. This effect becomes more pronounced as the clamping plates are approached. The maximum values at the centre line are reached at a distance equal to the width of the plate or rather less, and the change to an approximately parabolic distribution occurs at a ratio of length to width of less than 2 and greater than 3/2. The minimum values are not always at the centre, but a very small alteration of the grip of the bars, or in the judgment of the stress at which total extinction takes place, is sufficient to account for the distortions shown. Table X shows that the errors of observation and setting are somewhat variable, and are greater at longer lengths. This latter circumstance may be partly accounted for by the want of uniformity in the application of the load at the ends of the full length.

Table X.

Length of specimen.	Applied shear stress.	Mean tension stress.	Tension stress ÷ shear stress.	Percentage difference from the theoretical value.
inches.	lbs./sq. in.	lbs./sq. in.		
10	798	1513	1·88	−6·0
6	798	1546	1·94	−3·0
4	798	1567	1·96	−2·0
3	798	1570	1·97	−1·5
2	798	1570	1·97	−1·5

The rapid change in the intensity of the shear at the ends of the shear plates, and the apparent similarity of these portions of the curves for different lengths, is one of considerable interest, and it is important to enquire if the shear distributions follow the same general law for all lengths. The methods of experiment adopted for the general survey of a long plate do not adapt themselves very well for a very detailed examination of small areas, but the experimental values recorded afford some opportunity of testing the character of the end distribution curves, and it appears that the observations for a plate in which the ratio of length to breadth is in the neighbourhood of unity follow a parabolic law approximately. This may be shown by comparing the observed values with the corresponding values of a true parabola, and this has been carried out for a thick plate by applying Simpson's rules to obtain the areas of the experimental shear curves. In this way the mean average values of the shear stress have been found along the central lines of plates of square form, ½ inch, 1 inch, and 2 inches side respectively. These values are approximately 1413 lbs., 1560 lbs., and 1556 lbs. respectively, and correspond to parabolic distributions with maximum ordinates of 1·5 these average values.

True parabolic curves were plotted and compared with the experimental values, and one is shown in the accompanying fig. 15, from which it appears that the correspondence is a fairly close one.

The accompanying Table XI, showing approximately the percentage difference from a parabolic distribution, indicates a very fair agreement, with the exception of two observations at points close to the edges of the plate.

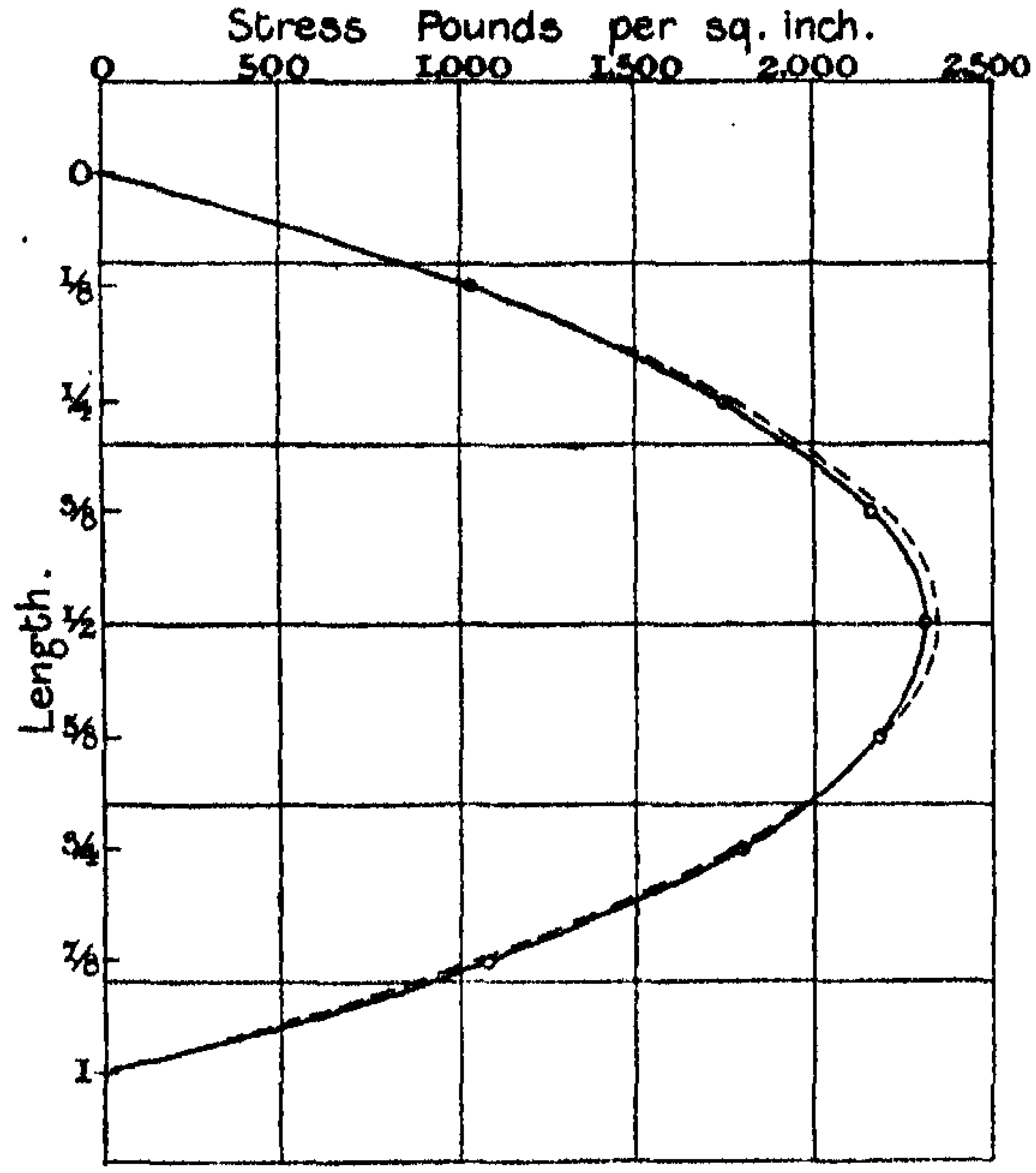

FIG. 15.

Table XI.

Distance from top edge, measured as a fraction of the length.	Percentage difference from parabolic law. Plate 0·186 in. thick.		
	½ in. × ½ in.	1 in. × 1 in.	2 in. × 2 in.
0	0	0	0
⅛	−0·2	−0·1	− 2·5
¼	−1·6	−0·3	− 2·3
⅜	−1·9	−2·3	− 8·5
½	+4·5	−1·4	+ 0·3
⅝	−2·5	0	− 3·4
¾	−8·2	+2·9	− 8·0
⅞	+5·4	+4·7	+19·0
1	0	0	0

As the length increases compared with the breadth the experiments show divergences from a parabolic distribution at the ends, and it seems probable that the law of change is of a more complicated character.

General Conclusions.—In deducing the main results of these experiments it is clear that the determinations at a high stress and at a low stress do not involve any differences of fundamental importance, since there is a very fair agreement throughout, and it is only in details and not with respect to the general distribution of the shear stress that there is any want of uniformity in the results.

It is shown that the shear stress in a long thin plate, subjected to a uniform shear load applied to the long parallel edges, rises rapidly from a zero value at each end to a maximum value, which latter is usually attained at a distance rather less than the free breadth of the plate; the stress then decreases in value until it reaches a minimum at the centre.

As the length of the plate is diminished, the maximum and minimum stresses become more pronounced, and when the ratio of the length of the plate to the free width is in the neighbourhood of two the distribution changes in such a manner that there is a maximum at the centre and a rapid fall to the ends.

The experiments show that a parabolic distribution of shear is probably only true within narrow limits. The distribution of shear stress over a long rectangular section may be approximately represented by a uniform shear over the central section with a rapid fall towards the ends. For rough approximations the shear stress over a long rectangular section may be taken as uniform throughout. The experiments appear to show that the distribution is of the same character for the same ratio of length to width.

In conclusion the author desires to express his warmest thanks to Prof. Karl Pearson, F.R.S., for his valuable advice and assistance during the progress of the work, and also to Prof. Silvanus Thompson, F.R.S., for much help in optical matters.

Spectroscopic Observations: Lithium and Cæsium.

By P. V. Bevan, Sc.D., Royal Holloway College.

(Communicated by Sir J. J. Thomson, F.R.S. Received January 4,—
Read February 8, 1912.)

[Plate 9.]

The present communication deals with a further study of the absorption spectra of the vapours of lithium and cæsium. These spectra were investigated, and the results communicated at the beginning of last year to the Royal Society.* The present account deals with an extension of the principal series lines for the two metals, and a more detailed examination of the expression of the wave-lengths by a formula, as well as an investigation of the broadening effect in a pair of lines with increase of density of the vapour of cæsium.

We shall deal first of all with the lithium spectrum. As has been remarked before, lithium vapour presents some difficulties, because of the high temperature required and the action of the vapour in this condition on the material of the containing vessel, but this difficulty can be surmounted by the use of a double steel tube and a large quantity of lithium. With the tube at a bright red heat, a dense enough vapour is produced to show in transmitted light a large number of the principal series lines; the number that can be observed depends, I am convinced, only on the resolving power of the spectrograph used to investigate them. With the instrument at my disposal, I have been able to measure 41 of these lines, and I think in this case the resolution has been pushed as far as is practicable, the last few lines being separated by only about 0·2 Ångström unit. Fig. 1, Plate 9, shows the absorption lines up to No. 25. The finer lines after this do not appear in the reproduction.

The following table gives the results of measurements. In the first column is the number of the line in the series. The second column gives the wave-length in International units founded on the absolute measurements of the red cadmium line. The next column contains an estimate of the possible errors in the individual wave-lengths. The fourth column gives the "oscillation frequencies" *in vacuo*—the number of wave-lengths per centimetre; and the last column the differences, observed — calculated values, the calculated values being those obtained from a Hicks formula to be discussed later.

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* 'Roy. Soc. Proc.,' A, vol. 85, p. 54.

Table I.—Lithium.

	λ.	Possible error in λ.	$10^8\lambda^{-1}$ *in vacuo.*	O – C.		λ.	Possible error in λ.	$10^8\lambda^{-1}$ *in vacuo.*	O – C.
1	6708 ·0	0 ·2	14903 ·5	0	21	2311 ·0	0 ·3	43258 ·2	–0 ·08
2	3232 ·66	0 ·03	30925 ·4	0	22	09 ·9	0 ·3	78 ·8	–0 ·15
3	2741 ·29	0 ·03	36468 ·7	0	23	8 ·9	0 ·3	97 ·5	–0 ·24
4	562 ·52	0 ·03	9012 ·7	+0 ·07	24	8 ·2	0 ·3	310 ·7	–0 ·14
5	475 ·05	0 ·1	40391 ·1	–0 ·11	25	7 ·4	0 ·3	25 ·7	–0 ·28
6	25 ·47	0 ·1	1216 ·7	–0 ·08	26	6 ·82	0 ·4	36 ·6	–0 ·18
7	394 ·46	0 ·2	750 ·5	–0 ·02	27	6 ·40	0 ·4	44 ·5	–0 ·03
8	73 ·8	0 ·3	2114 ·1	+0 ·09	28	5 ·82	0 ·3	55 ·4	–0 ·11
9	59 ·3	0 ·3	372 ·9	+0 ·22	29	5 ·36	0 ·3	64 ·0	–0 ·11
10	48 ·4	0 ·3	569 ·5	+0 ·03	30	4 ·94	0 ·3	71 ·9	–0 ·11
11	40 ·4	0 ·3	715 ·0	+0 ·08	31	4 ·58	0 ·3	79 ·7	–0 ·15
12	34 ·2	0 ·3	828 ·4	+0 ·12	32	4 ·24	0 ·3	85 ·1	–0 ·10
13	28 ·9	0 ·4	925 ·8	–0 ·28	33	3 ·95	0 ·3	90 ·5	–0 ·07
14	25 ·1	0 ·3	996 ·5	–0 ·13	34	3 ·68	0 ·3	95 ·6	–0 ·06
15	21 ·8	0 ·4	3057 ·1	–0 ·20	35	3 ·41	0 ·3	400 ·7	–0 ·12
16	19 ·2	0 ·4	105 ·3	–0 ·15	36	3 ·19	0 ·3	04 ·8	–0 ·05
17	17 ·0	0 ·3	146 ·2	–0 ·12	37	2 ·98	0 ·3	08 ·8	–0 ·03
18	15 ·1	0 ·3	181 ·6	–0 ·15	38	2 ·78	0 ·3	12 ·6	–0 ·03
19	13 ·5	0 ·5	211 ·5	–0 ·15	39	2 ·54	0 ·3	17 ·1	–0 ·08
20	12 ·1	0 ·5	37 ·6	–0 ·17	40	2 ·38	0 ·3	21 ·1	–0 ·12
					41	2 ·15	0 ·3	24 ·5	–0 ·13

The measurements for the lines 1—7 are by Kayser and Runge; 8 and 9 were measured by Liveing and Dewar, but were remeasured; 10—27 were given in my former paper already referred to; 28—41 are new. The errors indicated as possible are probably in nearly all cases much outside the limits. They have been increased for the lines 10—27, owing to the fact that the uncertainties in the measurements of the lines and in the determinations of the wave-lengths were under-estimated. To begin with, there is some considerable uncertainty in the values of the wave-lengths of the cadmium lines. For example, the values of the possible errors given by Kayser and Runge for the lines 2321·23, 2312·95, and 2306·72, are 0·20, 0·15, and 0·3, and when the cadmium spark is used as the source of light these lines are much over-exposed in the photographs, so that their positions cannot be determined with any great accuracy. Then there is some uncertainty in the Rowland standards on which the measurements of the cadmium lines are based. At present, Kayser has not extended the third order standards into this region, so that we have only the second order standards of Fabry and Buisson to go on, but there may easily be irregular errors of some hundredths of an Ångström unit in the old Rowland standards. As far as my actual measurements are concerned there should not be, in the case of lines not very near to cadmium lines in wave-length, errors of more than a few hundredths of an Ångström unit for lines near the end of the series, even when possible unsymmetrical broadening and other effects are taken into account. Taking all sources of error into consideration, I have put the possible errors high; the differences are due to the uncertainty when an absorption line is near an emission line, so that the true centre of each is difficult to determine. After the 25th line the measurements are expressed to hundredths of an Ångström unit, because, although the possible error is much above this order, yet, as a rule, the errors will affect lines almost equally, in so far as they are produced by uncertainty in the measurements of the position of the cadmium reference lines. The difference of wave-length between successive lines is thus much more accurately determined than the actual values.

In reducing the measurements to the International scale, the values of iron lines as determined by Fabry and Buisson were used; a table of the necessary corrections has been published by Birge* which gives practically the corrections used for Table I. The reduction to *vacuo* for the oscillation frequency was obtained from the list of corrections published in Watts' Index and the temperature corrections in the same volume.

The formula on which the last column of Table I is based is that due to Hicks

$$n = A - \frac{N}{(m+\mu+\alpha m^{-1})^2},$$

where n is the oscillation frequency, N the universal Rydberg constant, and m takes the values 1, 2, 3, etc., for the different lines of the series, A, μ and α being constants for the particular substance. Using the oscillation frequencies based on the International scale, we have to use a different value of N. The value has been calculated by Birge in the paper referred to from the wave-lengths of five hydrogen lines. This value is 109678·6 instead of the value 109675. Using the first three lines of the series to calculate the constants, we obtain

$$A = 43484{\cdot}3 \qquad \mu = 0{\cdot}951431 \qquad \alpha = 0{\cdot}007522,$$

and these values are used for the last column of Table I. The possible errors work out to be practically the same as those given by Hicks† for A ± 1·16, for $\mu \mp 0{\cdot}000326$, for $\alpha \pm 0{\cdot}000299$.

If we take a higher member of the series to determine A with approximate values of μ and α, the method I have used before‡ and adopted by Birge, we obtain a higher value of A; for example, from the lines 25, 30, 35, 40, we obtain the numbers 43488·6, 43486·4, 43485·6, 43486·5, but in each case a possible error ±5·7. This method does not give us such close limits as the method of taking the first three lines of the series if the limits of error are reliable. A slightly higher value of A would make the numbers in the column O−C look better, but the agreement would not be so good in the earlier members of the series, and in view of the larger possible errors in my own measurements, which quite possibly may all be too small, it is preferable to rely on the Kayser and Runge measurements for the earlier lines. The only line for which there is not agreement between the calculated and observed values is 4, for which the limit of error is given by Kayser and Runge as 0·03 and the difference appears as 0·07. This, probably, is to be explained by an error in the determined wave-length owing to errors in the old standards. It is quite possible that an error of 0·04 may be introduced owing to this. The agreement in the other lines is fairly complete.

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* R. T. Birge, 'Astrophys. Jour.,' vol. 32, p. 113.

† 'Phil. Trans.,' A, vol. 210, p. 96.

‡ 'Roy. Soc. Proc.,' A, vol. 83, p. 425.

Cæsium.

In former measurements of the absorption lines of cæsium vapour the absorption atmosphere was obtained by heating cæsium chloride with metallic sodium or potassium. Sufficient cæsium was set free to give a vapour which showed 24 of the absorption lines belonging to the principal series, but owing to the comparatively easy volatilisation of the sodium or potassium the spectrum was complicated by the presence of the sodium or potassium absorption spectrum.

A method of obtaining cæsium by heating the anhydrous chloride *in vacuo* with metallic calcium was given by Hackspill.* This method I found not very satisfactory for my purpose, as it was difficult to control the rate of formation of the cæsium. A more suitable method was found in heating the anhydrous chloride with metallic lithium. The lithium volatilises with difficulty, and a steady atmosphere of cæsium vapour of sufficient density can easily be maintained.

With this method the series lines were photographed up to the thirty-first of the principal series, and again the limit is only imposed by the resolving power of the instrument. The principal series for all the alkali metals, with the exception of lithium, consist of pairs of lines, the separation of corresponding pairs being greater as we go from sodium to cæsium. The lines are not equally intense in all cases, the line of greater wave-length in a pair being the less intense. There are, in fact, two series, P_1, P_2, in the notation of Rydberg. It is only in the cases of rubidium and cæsium that we could expect to be able to distinguish the pairs for more than a few members of the series, as, on the assumption that the two series have the same limit, the pairs become so close together that they cannot be separated. But in the case of cæsium especially the separation is considerable, and so the pairs of lines can be more easily distinguished. The later members in all these series belong to the P_1 series —this becomes clear from the cases of rubidium and cæsium, where the intensity of the P_2 lines falls off with higher order in the series until the line cannot be observed, although its position assuming an approximate formula should be quite easily distinguishable from the corresponding line of P_1. The lines of P_2 cannot be brought out by increase of density of the vapour, as this produces broadening of the P_1 lines, which spread over the position of the P_2 lines in the photograph. This disappearance of P_2 lines has led to some errors in applying formulæ to the series. Birge[*] has calculated constants for the Ritz formula for the alkali metals and has found that the formula is inapplicable in the case of cæsium, but the explanation is that for the first four members he has used P_2 lines—those of the pairs with greater wave-length—while the rest of the wave-lengths are of P_1 lines. The wave-lengths used by him for the higher members have not much accuracy, but the formula would give very much better results if the four lines of less wave-length were used. The same remark applies to all of Birge's calculations—he has used the P_2 lines where they are observed, while after the first few members it is the P_1 lines which are measured. This makes very little difference in the case of sodium, where the pairs are very close together after the first three—the only ones which have been observed. In the case of potassium also five pairs have been observed and for later pairs the differences would be hardly greater than the errors in the experimental numbers. For rubidium the differences are greater, and again this accounts for the bad fit for the numbers calculated by Birge from the Ritz formula.

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* 'Comptes Rendus,' 1905, vol. 141, p. 106.

In Table II are given the wave-lengths on the International scale. The first column gives the number in the series, the second the wave-lengths, the third the possible error, the fourth the oscillation frequency *in vacuo*, and the fifth the values of observed—calculated wave-lengths, to be dealt with later.

In Table II the wave-lengths for the first pair are measured by Lehmann. There are no other measurements which give a check on his values, but judging from his measurements of other lines in this infra-red region we can accept them as being reliable. The measurements for the second pair are by Kayser and Runge, and the values agree with those of Ramage and Exner and Haschek. The rest of the lines are my own measurements. For P(3) my value agrees with Kayser and Runge's (reduced to Inter-

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[*] *Loc. cit.*

Table II.—Principal Series Lines for Cæsium.

	λ.	Possible error in λ.	$10^8\lambda^{-1}$ *in vacuo.*	O – C.		λ.	Possible error in λ.	$10^8\lambda^{-1}$ *in vacuo.*	O – C.
1	8949·67	0·76	11170·7	0	12	3245·91	0·2	30799·8	–0·16
	8527·50	0·32	11723·6	0	13	37·47	0·2	879·4	–0·07
2	4593·16	0·05	21765·5	0	14	30·58	0·2	945·3	–0·09
	4555·26	0·05	21946·5	0	15	25·00	0·2	998·8	0
3	3888·65	0·15	25701·9	0·04	16	20·23	0·2	31044·8	–0·09
	3876·89	0·2	25788·6	0·17	17	16·34	0·2	82·3	–0·03
4	3617·41	0·15	27637·3	0·13	18	12·91	0·2	115·5	–0·09
	3611·52	0·2	27681·4	0·05	19	10·07	0·2	43·0	–0·08
5	3480·13	0·15	28727·1	0·09	20	7·67	0·2	66·3	–0·02
	3476·88	0·2	28753·2	–0·10	21	5·53	0·2	87·1	–0·02
6	3400·00	0·15	29403·4	0	22	3·60	0·2	205·0	+0·01
	3398·14	0·2	29419·5	0·13	23	2·02	0·2	21·3	–0·02
7	3348·72		29852·8	–0·09	24	0·60	0·2	35·2	+0·01
	3347·44	0·2	29865·0	–0·12	25	3199·84	0·2	47·5	+0·03
8	3314·04	0·2	30165·2	–0·09	26	8·14	0·2	59·2	–0·01
	3313·16	0·2	30174·0	–0·05	27	7·17	0·2	68·7	+0·05
9	3289·13	0·2	30392·2	–0·25	28	6·09	0·2	79·2	–0·11
	3288·56	0·2	30399·8	–0·16	29	5·31	0·2	86·9	–0·05
10	3270·44	0·2	30568·1	–0·16	30	4·48	0·2	95·0	–0·13
11	56·66	0·2	697·5	–0·15	31	3·83	0·2	31301·3	–0·10

national units)—3888·69—but their value for the other one of the pair is 3876·59, with a possible error of 0·1. Ramage gives 3876·31, which agrees better with my own value, and would give better agreement with the calculated values. I have kept my own value, as it seems certain that the Kayser and Runge value is too high. For P(4) Kayser and Runge's values are 3611·69, 3616·93; corrected to international units Ramage gives 3611·55, 3617·34; Kayser and Runge's limits of error are given as 0·3 and 0·2 respectively. For my own measurements the line of greater wave-length was very fine, the breadth being about 0·05; the other line was broader, about 0·2 unit. It seems probable that Kayser and Runge's value for $P_2(4)$ is too low. Ramage for $P_1(5)$ gives 3477·10, and for succeeding lines 3398·30, 3348·59, 3314, 3287. The line $P_2(7)$ has no error attached to it, as it is practically coincident with a rubidium line 3348·72 which always appeared in the photographs, the two lines appearing together simply as one. It is doubtful therefore what this measurement represents.

For the determination of the constants A, μ, α, of the Hicks formula

$$n = A - \frac{N}{(m+\mu+\alpha m^{-1})^2},$$

the method adopted was to take a fairly high order of line for P_1, 15, which with approximate values of μ and α determines A. Then from two early lines μ and α can be redetermined. Successive approximations give very quickly the constants required. For P_2 the sixth line was used and the first two. The work of approximation is, of course, slower than for P_1, but not much arithmetic is involved. The possible errors in the constants are determined as by Hicks, and it easily appears that the best results are obtained by using the first two lines. We obtain, using for P_1 the lines 1, 2, and 15,

$$A = 31404{\cdot}6 \pm 1{\cdot}5,$$

$$\mu = 1{\cdot}449975 \mp 0{\cdot}000582, \qquad \alpha = -0{\cdot}089294 \pm 0{\cdot}000516$$

(using 2, 3, and 15 we obtain

$$\mu = 1{\cdot}448594 \mp 0{\cdot}002514, \qquad \alpha = -0{\cdot}086532 \pm 0{\cdot}004596).$$

For P_2 we obtain, using 1, 2, and 6,

$$A = 31404{\cdot}6 \pm 1{\cdot}9,$$

$$\mu = 1{\cdot}418206 \mp 0{\cdot}000714, \qquad \alpha = -0{\cdot}090002 \pm 0{\cdot}000674.$$

The two values of A for P_1, P_2, come out the same, which is in agreement with the assumption that the two series have the same limit. This is, I think, the best evidence for this relation between the pairs that we have at present. The column O − C in Table II gives the differences between the observed and calculated values of the wave-lengths derived from these values of the constants. The agreement is everywhere within the experimental limits of error except for $P_2(9)$. A permissible change in A would bring this inside the limits, but in any case it is not a very reliable observation—it is the last of the P_2 series visible, and so a very faint line, difficult to pick out and measure. Perhaps a greater error should have been allowed in this case, but, as is hardly necessary to say, the possible errors were allotted before the calculated values were obtained.

The values of the constants μ and α enable us to make more complete the investigation with regard to the relations they exhibit through the series of the alkali metals. For this purpose I have recalculated the constants of the P_1 series for sodium, potassium, and rubidium, reducing the wave-lengths to the International scale and to *vacuo*. The reduction is not very satisfactory, as for the infra-red we have to extrapolate, but it seemed worth while to make the attempt to get as near the right values as possible. The following table gives the values of μ and α with limits of error for the four metals Na, K, Rb, Cs, for the P_1 series:—

	μ.	α.
Na	$1{\cdot}148261 \pm 0{\cdot}000549$	$-0{\cdot}031432 \mp 0{\cdot}000479$
K	$1{\cdot}296116 \pm 0{\cdot}001199$	$-0{\cdot}061508 \mp 0{\cdot}000510$
Rb	$1{\cdot}366300 \pm 0{\cdot}000588$	$-0{\cdot}074476 \mp 0{\cdot}000268$
Cs	$1{\cdot}449975 \pm 0{\cdot}000582$	$-0{\cdot}089294 \mp 0{\cdot}000516$

These numbers were calculated from the lines 1, 2, and 35 for sodium, with a slight increase in possible errors owing to uncertainty in the old Rowland standards—an increase of this kind has been made in all cases. For potassium the lines 1, 2, and 22 were used, and for rubidium 1, 2, and 25. The limits are on the whole narrower than those given by Hicks. In the case of sodium the limits are wider owing to the fact that the published possible errors have been increased for the reason mentioned above.

It follows at once from these numbers that the relations* for $\mu-1$, α, and $\mu+\alpha-1$ are not exact; we have in fact the following:—

	$\mu-1$.
Na	2 (0·074131 ± 0·000275)
K	4 (0·074029 ± 0·000300)
Rb	5 (0·073260 ± 0·000118)
Cs	6 (0·074996 ± 0·000097)

	$\alpha/(\mu-1)$.	$\mu+\alpha-1$.
Na	0·2120 ± 0·0040	2 (0·058415 ± 0·000058)
K	0·2081 ± 0·0071	4 (0·058652 ± 0·000139)
Rb	0·2033 ± 0·0011	5 (0·058365 ± 0·000028)
Cs	0·1980 ± 0·0020	6 (0·060113 ± 0·000019)

We see in the values of $\alpha/(\mu-1)$ a regular decrease with increasing atomic weight, but clearly the fraction is not constant. In the values of $\mu-1$, however, there is no apparent relation to the atomic weights. It also appears that it is impossible to make the fraction $\alpha/(\mu-k)$ when k is different from 1 a constant multiplied by the numbers 2, 4, 5, 6. An expression of the form

$$\mu+\frac{\alpha}{m} = 1-\mathrm{W}\left(1-\frac{1}{m}\right)+0{\cdot}074560\,s\left(1-\frac{0{\cdot}21521}{m}\right)$$

is given by Hicks† which applies to Na, K, and Rb, and to Cs if the W term is dropped. This expression also is not exact within the limits prescribed. It agrees for the part independent of m for Na, K, and Rb but the part representing α is outside the limits for Rb, and the numbers when the term in W is dropped cannot be made to agree with μ and α for cæsium. These relations then cannot be considered as exact, although they are very suggestive and provide fairly good approximations to the actual lines. We can therefore only regard the formulæ based on them as being approximations. It would doubtless not be difficult to add other terms to the Hicks expressions depending on the atomic weights or other properties of the metals and thus obtain expressions correct within the limits prescribed, but there seems little point in attempting this at the present stage, as Hicks' own expressions are so near the actual values that new terms would be so small and the possible errors so large that we could conclude nothing as to their real correspondence with the actual state of affairs and they would be mere interpolation terms.

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* Hicks, *loc. cit.*, p. 77 f.

† *Loc. cit.*, p. 80.

Broadening of Lines with Increase of Density of Vapour.—Absorption lines are never quite as sharp as good emission lines, though in some cases their apparent breadth can be certainly less than 0·01 Å.U., and therefore there is some doubt in measurements of wave-lengths by means of absorption, as errors may be introduced owing to the broadening of the line not being symmetrical. It seemed worth while therefore to examine a typical case with some care to see the effect firstly on the determination of wave-length, and secondly for the interest of the asymmetry of the broadening itself. It is observed that in all cases with these principal series lines the broad line obtained by using dense vapour behaves in the same way. The line broadens unsymmetrically, extending much further on the more refrangible side than on the other. As all the lines I have observed behave in a similar way a careful examination of one pair was made, and for this purpose the second pair in the cæsium series was investigated. The advantages of taking this pair were that it occurs in a visible part of the spectrum, so that ordinary glass for lenses and prisms could be used, and also that the effect on each line could be studied, as the two lines are separated by a considerable interval.

To get more dispersion for this case a small Thorpe grating mounted on a prism to form a direct vision spectrograph was used. The effective aperture was somewhat less than 2 cm. This was mounted on an ordinary laboratory spectrometer and the telescope was replaced by a camera. The mounting of the apparatus left a great deal to be desired in the way of rigidity, but some satisfactory photographs were obtained. Fig. 2 of the plate shows enlargements of the photographs obtained: (1) shows the absorption using a white source of light—a Nernst lamp; (2) has the iron arc photographed in addition to the absorption spectrum. With the apparatus used it was very difficult to keep the adjustment when changing from the absorption spectrum to the comparison spectrum. However, as the series of photographs shows, with a certain number of failures there were obtained some good results. From a glance at the figure the asymmetry of the effect can at once be seen. Measurements were made of the edges of the lines—the edge of the line is of course somewhat indefinite as there is no abrupt change, but measurements of the two edges are probably fairly comparable, as,

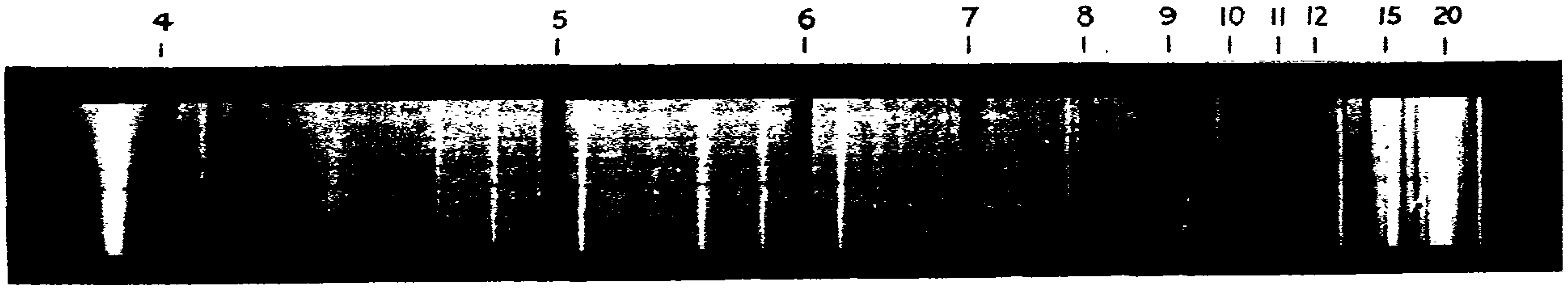
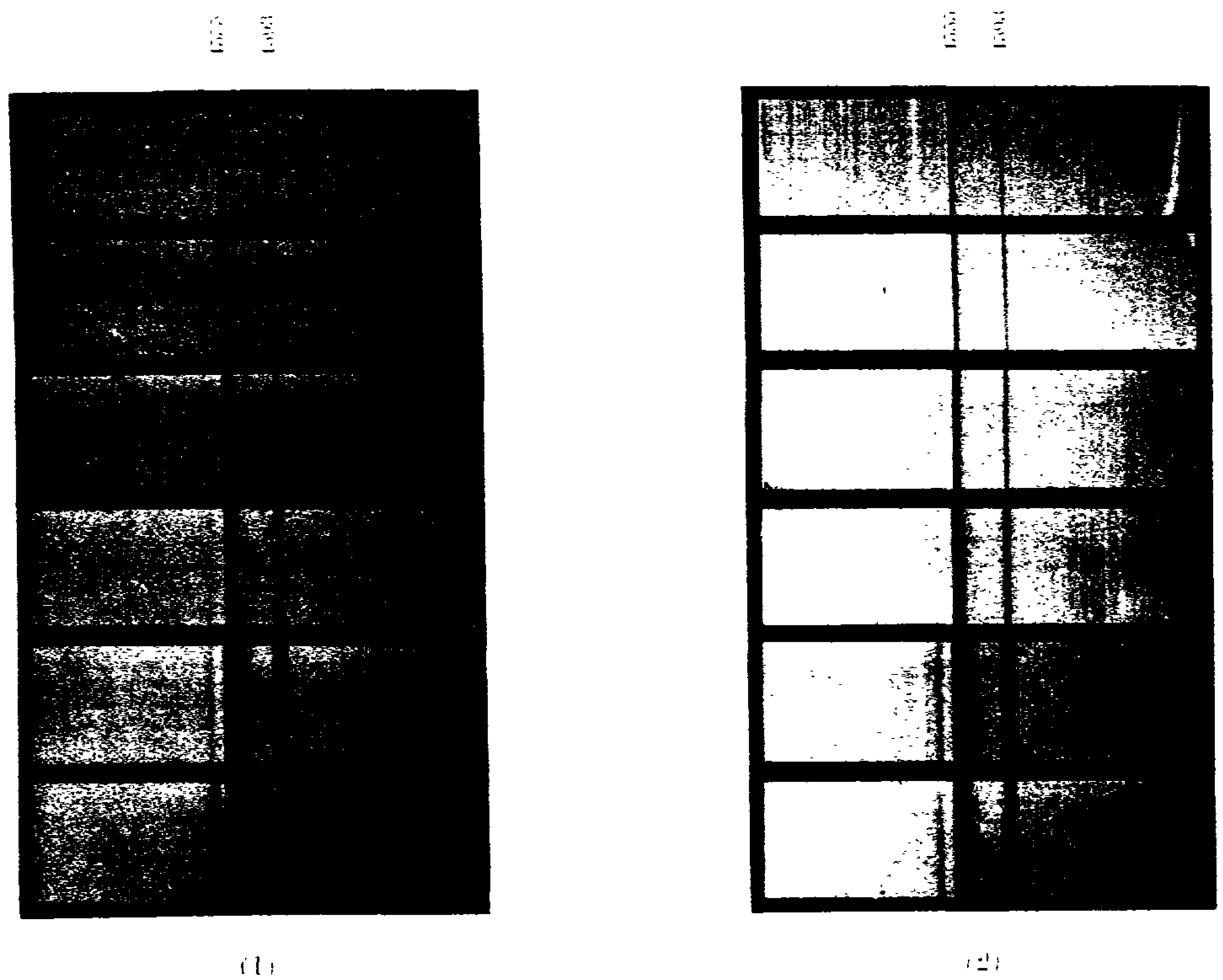


Fig. 1.


(1)

(2)

Fig. 2.

at any rate until the line becomes very broad, the aspect of the two edges is practically the same. The following table gives a set of measurements of the two edges of these lines:—

4555·26.		4593·16.	
4555·25	4555·78		
55·00	56·23	4593·17	4593·58
54·90	57·14	92·96	93·79
54·74	57·73	92·91	94·20
54·11	59·06	92·91	95·08
53·99	61·06	92·55	95·74
54·12	61·09	92·55	95·59
53·9	70·0	92·3	600·0

The wave-lengths were determined from the iron lines 4531·16, 4602·94. The second of these was not a good line, and there may easily be in some of these measurements an error of 0·1 Å.U. from this cause, but in any case it is clear that the broadening is very much more on the side of greater wave-length. The narrowest lines of the above were considerably broader than those used in wave-length determinations. The broadening effect is greater in the earlier members of the series, and the lines after the first few of the early members remain very fine, except in the case of very dense vapour. For example, in the case of one of the photographs from which $CsP_2(4)$ was determined, the breadth of the line was less than 0·05 Å.U. In all cases of lines used for measurement the breadth of the lines was not greater than 0·15 Å.U., and in most cases not greater than 0·07. From the above table it is clear that the centre of the absorption line will give too great a wave-length, but the effect is not large enough for account to be taken of it with the accuracy available for my measurements.

The So-called Thermoid Effect and the Question of Superheating of a Platinum-Silver Resistance Used in Continuous-flow Calorimetry.

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In a recent paper by Glazebrook, Bousfield, and Smith* some doubt has been cast on the accuracy of my absolute measurements of the specific heat of water by the continuous-flow calorimeter. It is stated that an error of as much as 6 parts in 10,000 might have occurred in the superheating of the oil-stirred platinum-silver resistances from which the values of the electric heating current were obtained. On the other hand, it is also stated that this error might have been as small as 2·5 parts in 10,000. It was with some surprise that I read this statement, inasmuch as the authors could not have been aware of the rapidity of oil circulation which I used. It has been shown by Osborne Reynolds and others that the heat loss from a surface immersed in a liquid moving in turbulent motion is directly proportional to the velocity of flow. The degree of superheating of a wire immersed in oil will depend then directly on the rate of circulation. Fully realising this fact, the resistances which I used were designed by Prof. Callendar and myself to be immersed in oil which could be circulated with great rapidity. These resistances are described in our papers,† where the illustration shows approximately to scale the relative sizes of the stirrer and resistances. The paddle was rotated at a high speed by a powerful water motor, and the oil was thrown down with such force that a considerable depression was made in the surface. The oil, thrown sideways, passed up around the bare wires, which were wound loosely on the mica frames. I do not know by what standard Glazebrook, Bousfield, and Smith decide what is "normal stirring" or "very vigorous stirring," but it was evident to me at once that I must have had much more rapid circulation than anything used by these authors.

In testing the accuracy of my experiments special attention was taken of possible superheating, and tests of stirring were made at the time. The good agreement of the various determinations of the specific heat, made with such different values for the heating current and flow of water, make it evident that no large superheating error could have existed without being detected.

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* 'Roy. Soc. Proc.,' 1911, vol. 85, p. 541.

† 'Phil. Trans.,' 1902, A, vol. 199, p. 55 and p. 149.

In spite of this, however, I have thought it worth while to test my resistances for superheating again. I have accordingly made up a platinum-silver resistance out of wire 0·06 cm. in diameter, rolled into a flat ribbon about 2·5 mm. wide and 0·0075 cm. in thickness. Four ribbons of this thin metal strip were taken, connected in parallel on an ebonite frame, and immersed in an oil bath with stirrer, the mounting being similar to the specific heat resistances. These ribbon strips were each approximately 150 cm. long. Hence the total cooling surface in contact with the oil was 75 sq. cm. per strip, giving a total of 300 sq. cm. and a resistance of approximately 1 ohm.

The old mica resistances consisted of two 1-ohm coils in parallel. For this comparison one coil (No. 2) was disconnected and No. 1 connected in series with the ribbon-strip resistance. Each of the old coils was made of four wires 100 cm. long and 0·04 cm. in diameter. Hence each wire had a cooling surface of 12·56 sq. cm. or a total surface of 50 sq. cm. for a resistance of 1 ohm. Thus it will be seen that the ribbon coil has six times as much cooling surface as coil No. 1. The oil in both boxes was circulated at the same speed from the same water motor, and this circulation was the same as that employed during the specific heat measurements. A steady heating current was passed through the coils and the temperature of the oil maintained steady in both boxes by means of coils of tube through which cold tap water was flowing. The drops of potential across the coils were compared on our Kelvin-Varley slide potentiometer. Both readings came very nearly at the same part of the slide. The errors of this potentiometer have recently been redetermined for me by Mr. A. N. Shaw, M.Sc., for his work on the absolute measurements of the Weston cell, and the constancy of the instrument is a matter of great interest and satisfaction.* The galvanometer used was the Broca type, from the Cambridge Scientific Instrument Company, with 1000-ohm coils, and gave a sensitiveness from 17 to 40 divisions of scale to one division of the vernier slide. The comparison could, therefore, be made with an accuracy of one or two parts in 100,000 with all the heating currents.

The following table gives the value of the ribbon coil calculated by assuming the correctness of coil No. 1 for all heating currents. The resistance of coil No. 1 was obtained by reference to the resistance temperature chart which was obtained with great care for the specific heat experiments.

* The results of this comparison will be published later.

Heating current.	Temp. of oil. Ribbon resistance.	Ribbon resistance.	Ribbon resistance reduced to 10°.	Difference in parts per 10,000.
amps.				
1·5	9·9	1·07604	1·07607	0
2·5	9·9	1·07601	1·07604	0·3
3·5	10·2	1·07609	1·07604	0·3
4·5	11·1	1·07622	1·07595	1·2
5·5	11·7	1·07640	1·07598	0·9

The last two values of the ribbon resistance in Column 4 show the existence of a small superheating of coil No. 1 over the ribbon resistance, but are for heating currents in excess of the greatest used in the specific heat experiments. The calculations made by Glazebrook, Bousfield, and Smith for my coils were for the maximum current used, which was 8 ampères divided between the two. This gives 4 ampères for each coil, or 1 ampère for each wire conductor. Since the ribbon resistances have a cooling surface six times as great as the standard we should expect a difference between the two coils of 5 parts in 10,000 were the Teddington method of stirring followed, while according to the Hendon stirring this should have been 2 parts in 10,000 for a heating current of 4 ampères. With the method of stirring we used the actual difference is seen to be not over 1 part in 10,000 for a development of heat twice as great. Taking the probable value for a current of 4 ampères the difference is only 5 parts in 100,000.

Quite apart from the close agreement of the individual observations of the specific heat of water for widely different heating currents, these comparisons justify me in concluding that the error due to superheating in my platinum-silver resistances is certainly not more and probably less than 1 part in 10,000, and therefore beyond the limits of error of the method of continuous calorimetry.

The Observation by Means of a String Electrometer of Fluctuations in the Ionisation Produced by γ-Rays.[*]

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A γ-ray is a projected entity, according to the theories of J. J. Thomson,[†] of Bragg,[‡] and of J. Stark,[§] and the effect of it will be localised in space in the sense that the effect of a bullet is. Any one of these theories requires the ionisation produced by γ-radiation in a gas at any instant to fluctuate both in space and time. In this respect the effect of γ-rays would be similar to that of α-particles; as is well known, the spinthariscope exhibits for the latter rays both fluctuations in time and discontinuity in space. Similarly, the effects predictable for β-rays have been observed, but, when the experiments recorded below were begun, no such fluctuation had been observed for γ-rays. In 1908 one of us described how they might be sought for experimentally: "At the same distance from a source of γ-rays, two identical and adjacent ionisation chambers would be placed to catch the γ-rays. With one chamber at $+v$ volts and the other at $-v$, the electrode of one receives positive ions, the other negative; connecting the electrodes, the electroscope would receive the small excess of ions of one sign. If the γ-radiation is a spherical wave surface, then the ionisations in the chambers will have a constant ratio. This is true . . . . even when the energy varies continuously over the wave front; the excess current to the electroscope is then to a first approximation constant. If, on the other hand, the γ-rays are particles emitted in random directions as α-rays are, then the number entering each chamber in the given time will fluctuate. In the extreme case, during a short time a few γ-particles might enter one chamber, and none the other. In the more general case, when some large number of particles enter both chambers, the current to the electroscope will fluctuate."[‖]

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[*] [The paper was forwarded from New Zealand on December 8, 1911, so that the more recent literature had not reached the authors.—Sec. R.S.]

[†] J. J. Thomson, 'Proc. Camb. Phil. Soc.,' 1907, vol. 14, Part IV, p. 423.

[‡] W. H. Bragg, 'Phil. Mag.,' 1907, vol. 14, p. 429.

[§] J. Stark, 'Phys. Zeit.,' 1910, vol. 11, p. 24.

[‖] Abstracted from the application, in 1908, for the Royal Society grant, which defrayed part of the expenses of this investigation.

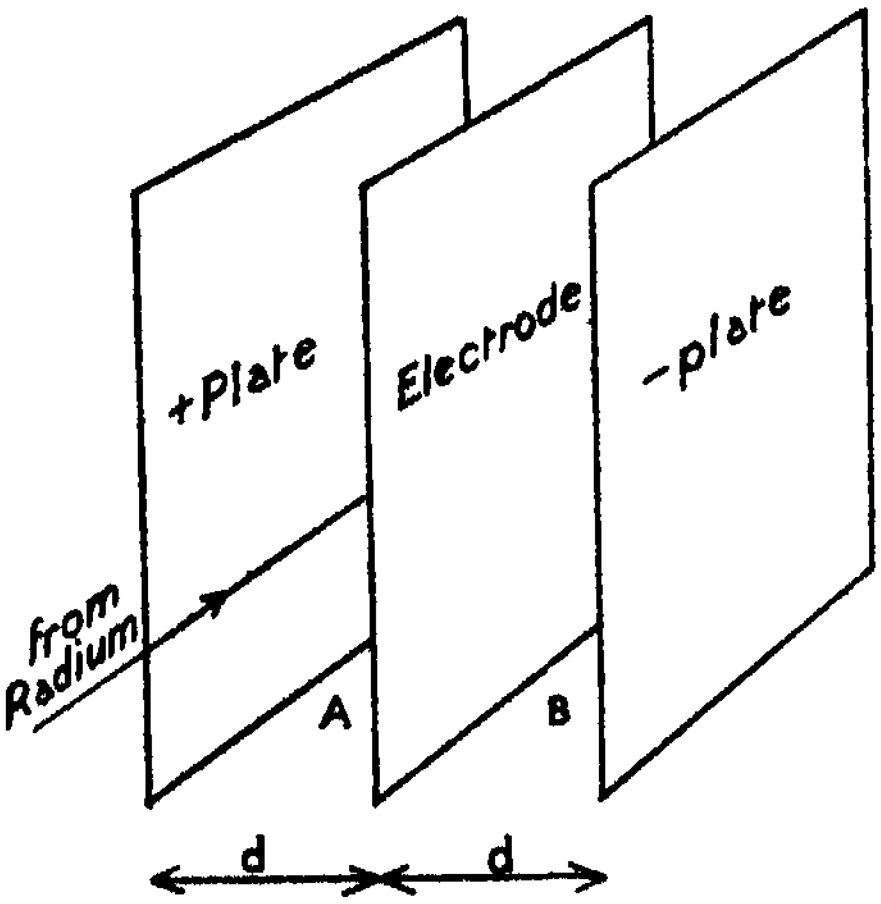

FIG. 1.

With the above arrangement, fluctuations have been observed in the ionisation produced by γ-rays. The two volumes of gas (see fig. 1) ionised were equal, and on opposite sides of one electrode, which collected the positive ions from one volume and the negative from the other; the radium, the source of the γ-rays, was equidistant from, and symmetrically placed with respect to, the two volumes. Yet the number of ions in the two volumes varied, sometimes one having an excess, sometimes the other. Spurious effects were eliminated with some difficulty; finally, however, the fluctuations ceased when the radium was removed. Thus the ionisation due to γ-rays is discontinuous in space; the discontinuity may be due to (1) the γ-rays being projected entities, or (2) a variation in the number of ions produced in a gas by the passage of a single γ-ray.*

Von Schweidler† in 1910 discussed in a theoretical paper the possibility of distinguishing between the continuous electro-magnetic pulse theory‡ and the projected entity (corpuscular) theories; he concluded that the counting of the elementary processes produced by γ-rays in a limited space constituted a crucial experiment. The experimental arrangements he proposed are indicated in fig. 2. The ionisation in C will fluctuate in intensity on either the pulse or corpuscular theory, for if the disturbance acting on C is a pulse it is discontinuous in time, if corpuscular both in time and space. Von Schweidler went on to consider how these elementary processes are to be detected and counted. As γ-rays do not give scintillations,[*] and Rutherford and Geiger's[†] method would probably fail, these two direct methods, which have been used for counting α-particles, are not available to count γ-rays. He suggested that an indirect method of counting γ-rays is afforded by his theory of the fluctuations which arise in the occurrence of any finite number of radioactive processes in accordance with the usual laws of chance.[‡] He thought, however, that the γ-rays may make too few ions for his theory to be experimentally realisable, for if the number of γ-rays, z, to be counted was sufficiently large to produce a discernible ionisation the fluctuation, E, which is proportional in absolute value to $\sqrt{z}$ (*i.e.* proportional to $1/\sqrt{z}$ of the whole ionisation), would be too small to measure. But in this relation we have, theoretically at any rate, as Von Schweidler pointed out, a distinction between the two theories of γ-rays, assuming that the number of ions made by a γ-ray is constant and not itself subject to fluctuations.[§] This distinction may be best made clear by an account of Dr. Edgar Meyer's experiments.[||]

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* There is a good deal of evidence that γ-rays as such do not ionise, but that the ions are produced by the β-rays resulting from the γ-rays (see Bragg, 'Phil. Mag.,' September, 1910, p. 385).

† Von Schweidler, 'Phys. Zeit.,' March, 1910, vol. 11, p. 225.

‡ Stokes put forward in the Wilde Lecture this theory to explain Röntgen rays ('Proc. Manchester Lit. and Phil. Soc.,' July, 1897, vol. 41).

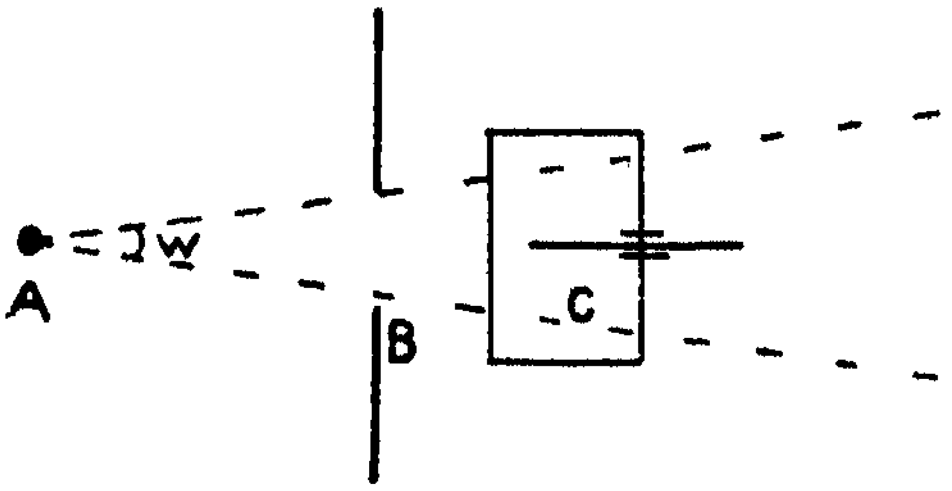

FIG. 2.—A, radium source of γ-rays; B, screen with variable aperture; C, ionisation can.

In the first of these experiments Meyer seeks to discriminate between the pulse and projected entity (corpuscular) theories of γ-rays by comparing the fluctuations in the ionisation in C (fig. 2) when using first a beam of γ-rays[¶] of solid angle ω and next of ω'. The fundamental distinction is that on the pulse theory the number of γ-rays entering C in a given time is on the average the same in the two experiments, while on the entity theory the number of γ-rays entering C is proportional to the solid angle.

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[*] Rubens, 'Phys. Zeit.,' 1909, vol. 10, p. 826.

[†] Rutherford and Geiger, 'Roy. Soc. Proc.,' August, 1908, A, vol. 81, p. 141.

[‡] E. von Schweidler, 'Int. Cong. de Rad.,' Liège, 1905; see abstract in 'Le Radium'; compare N. R. Campbell, 'Proc. Camb. Phil. Soc.,' February, 1909, vol. 15, p. 117, and 1910, pp. 310, 513.

[§] In a subsequent paper mentioned later von Schweidler investigated the theory of fluctuations for γ-rays without this assumption.

[||] E. Meyer, 'Berlin Berichte,' June, 1910, vol. 32, p. 647.

[¶] From 16·5 mgrm. of $RaBr_2$.

On the corpuscular theory

$$E_1/E_2 = ke\sqrt{z_1}/(ke\sqrt{z_2}) = \sqrt{(i_1/i_2)},$$

where E is the fluctuation in the ionisation, k the number of pairs of ions produced by each of the z γ-rays, e is the ionic charge, and i the saturation current. The suffixes refer to the screens used to limit the solid angle of rays. Thus, on the corpuscular theory, the ratio of the fluctuations in the two tests is equal to the square root of the ratio of the saturation currents, making the important assumption that the number of ions produced per γ-ray is constant. On the pulse theory, the number of ions produced by a pulse must depend on the portion of the whole disturbance that is allowed to act on the gas under observation. In this case we have

$$E_1/E_2 = K_1e\sqrt{z'}/(K_2e\sqrt{z'}) = K_1/K_2 = i_1/i_2,$$

where K is the number of ions produced by the effective portion of each of the z' γ-pulses.

Using three ratios of screen aperture, a large number of experiments gave—

E_1/E_2.	$\sqrt{(i_1/i_2)}$.	i_1/i_2.
1·01	1·19	1·41
1·44	1·38	1·88
1·28	1·28	1·50

These results support the corpuscular theory, for E_1/E_2 is clearly somewhat nearer in value to $\sqrt{(i_1/i_2)}$ than to i_1/i_2; but since the detailed results show large irregularities, improved arrangements were devised by Meyer, and a differential method used, the ionisation vessel being indicated in fig. 3. The fluctuations were measured with both A and B connected to the electrometer (E_G) and with A alone (E_H). In the first case on the pulse theory there should be no fluctuations (that is, $E_G = 0$), as the two parts of the vessel would be equally affected by the pulse, and

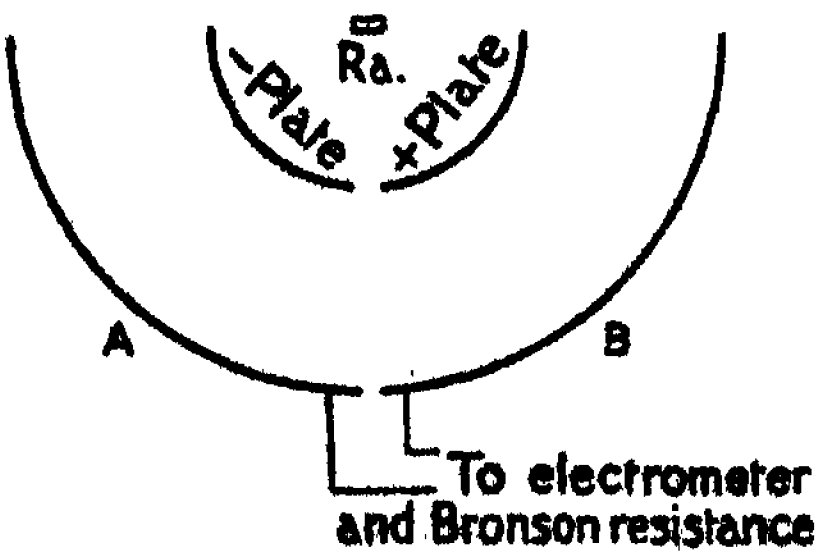

FIG. 3.

A would receive as many negative ions as B receives positive. On the corpuscular theory $E_G/E_H = \sqrt{2} = 1{\cdot}41$; actually the average value of E_G was 1/1000 of a volt, and $E_G/E_H = 1{\cdot}5$. But we think this result is open to objection for practical reasons mentioned later.

Finally, experiments were made to justify the assumption that the number of ions (k or K) formed by a single γ-ray is constant, for otherwise the fluctuations observed might have arisen from variations in k or K. Two experiments were made, the first with the ionisation vessel lined with aluminium and filled with carbon dioxide, and the second with the vessel lined with brass and filled with air, thereby altering the intensity and nature of the secondary rays from the walls and the number of ions formed per γ-pulse or corpuscle. *According to* Meyer *the ratio of the fluctuations* in the two experiments would be equal to the ratio of the saturation currents, if k is not subject to fluctuations, for then

$$E_1/E_2 = k_1e\sqrt{z}/(k_2e\sqrt{z}) = k_1/k_2 = i_1/i_2,$$

where k_1 and k_2 are the number of pairs of ions per γ-ray in the respective experiments. On this theory, then, $E_1i_2/E_2i_1 = 1$, and the observed value of E_1i_2/E_2i_1 in six experiments was 1·04, 0·93, 1·15, 1·02, 0·90, 0·99, mean 1·00; this warranted the assumption that the number of ions generated by a γ-ray in the vessel used was constant. In other words, it is concluded that, while a number of radioactive effects are subject to variations from the mean, the number of ions formed by a γ-ray is subject to no observable variation. It is interesting to note that von Schweidler came to precisely the opposite conclusion in a theoretical paper (see below) published after Meyer's, viz., that the fluctuation in the number of ions formed per γ-ray would exceed the fluctuation in the number of γ-rays in any ordinarily sized vessel, *for many γ-rays* would not ionise at all.

Several criticisms of Dr. Meyer's refined experiments would occur to anyone who has used a Bronson resistance and a quadrant electrometer, the instruments which he used to measure the fluctuations. The first is that no evidence is given to show how far spurious fluctuations produced by the Bronson resistance itself* by variations in the 1000 to 2000 volt battery used and mechanical tremors were eliminated. Many of the ions in the experiment of fig. 3 never reach either of the electrodes A or B, so it is not surprising that the largest fluctuation observed in that experiment was very small, being only 1/1000 volt. Further, the results of it are of no significance if this

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* Meyer and Regener, 'Verh. Deut. Phys. Ges.,' January 15, 1908. [This paper was sent to the Royal Society from New Zealand long before the authors could have become acquainted with the recent discussion of this subject.]

1/1000 volt was not quantitatively measured by the quadrant electrometer; no details are given of how such an unusual degree of refinement was obtained.

Dr. von Schweidler, in his second paper,* applied the theories of discontinuous phenomena developed by Mr. N. R. Campbell† to the experimental conditions indicated by fig. 2. He concluded that, if the γ-rays ionised indirectly,‡ then:—

I. For *corpuscular* radiation—

$$z_1 = z\omega/4\pi, \qquad k_1(m_1) = k(m),$$

$$\overline{\Delta^2} = \bar{z}\,\omega/4\pi\,.\,\bar{m}\bar{n}^2(\bar{m}+1) = \bar{Q}\bar{n}(\bar{m}+1).$$

II. For *pulse* radiation—

$$z_2 = z, \qquad k_2(m_2) = \omega/4\pi\,.\,k(m),$$

$$\overline{\Delta^2} = \bar{z}\bar{n}^2\{(\omega/4\pi\,.\,\bar{m})^2+\omega/4\pi\,.\,\bar{m}\} = \bar{Q}\bar{n}\{\omega/4\pi\,.\,\bar{m}+1\},$$

where $\bar{z}$ is the mean number of rays emitted by the source in all directions in a given time,

z is the actual number in a single experiment,

ω is the solid angle of the rays entering the ionisation chamber,

$\overline{\Delta^2}$ is the mean square of the fluctuation in the number of ions in the given time,

k is the number of pairs of ions generated per γ-ray,

m is the number of secondary rays generated in C (fig. 2) by one primary ray,

n is the number of pairs of ions generated by each secondary ray, thus $k = mn$,

$Q = zk$ is the number of ions of one sign liberated in the given time.

On Bragg's view of the process of ionisation by γ-rays $\bar{n}$ would be large compared to 1, and $\bar{m}$ small compared to 1. In that case the fluctuation on both the corpuscular and pulse theories is

$$\overline{\Delta^2} = \bar{Q}\bar{n}, \text{ approx.},$$

and no distinction between the two theories seems to be obtainable by such experiments as Meyer's. If von Schweidler's reasoning and Meyer's experiments are sound, then γ-rays do not ionise as Bragg supposes. Von Schweidler calculates that not 1 per cent. of the γ-rays passing 20 cm. of air would have any effect in it; and, consequently, the fluctuation in the number of γ-rays accidentally effective would exceed the fluctuations in the number entering the vessel.

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* Von Schweidler, 'Phys. Zeit.,' July, 1910, vol. 11, p. 614.

† N. R. Campbell, *loc. cit.*

‡ The theory of direct ionisation is also given.

Experimental Methods.

The experiments we have carried out on this question consist essentially in observing the fluctuations, during short periods of time, in the balance of two ionisation cans containing air exposed to the γ-rays from radium. The general arrangements will be seen from figs. 1, 4, 5 and 6.

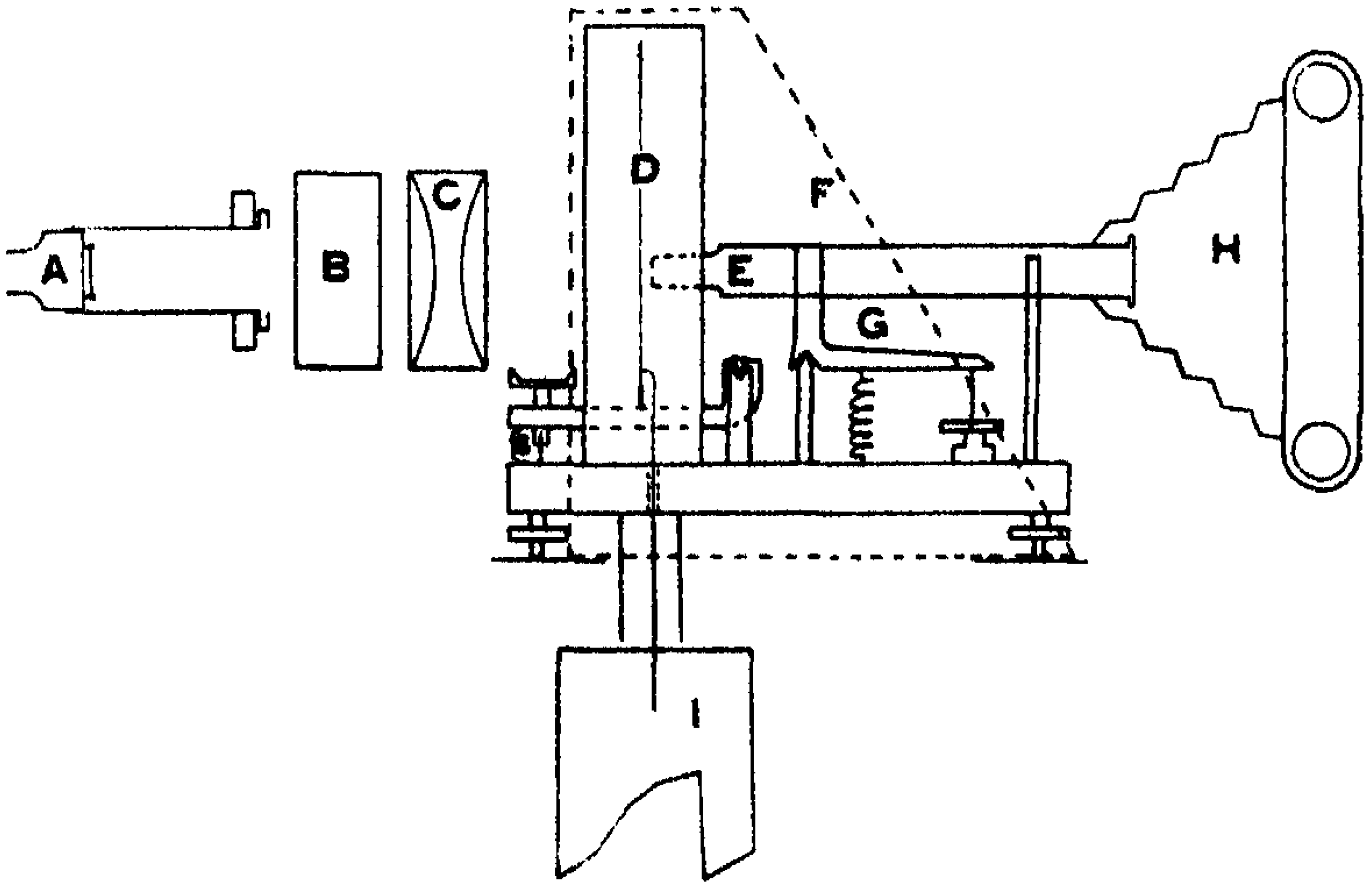

Fig. 4.—A, Nernst lamp; B, cell to absorb heat rays; C, condenser; D, quartz fibre of electrometer; E, microscope; F, lead shield; G, focussing mechanism for microscope; H, photographic camera; I, ionisation can.

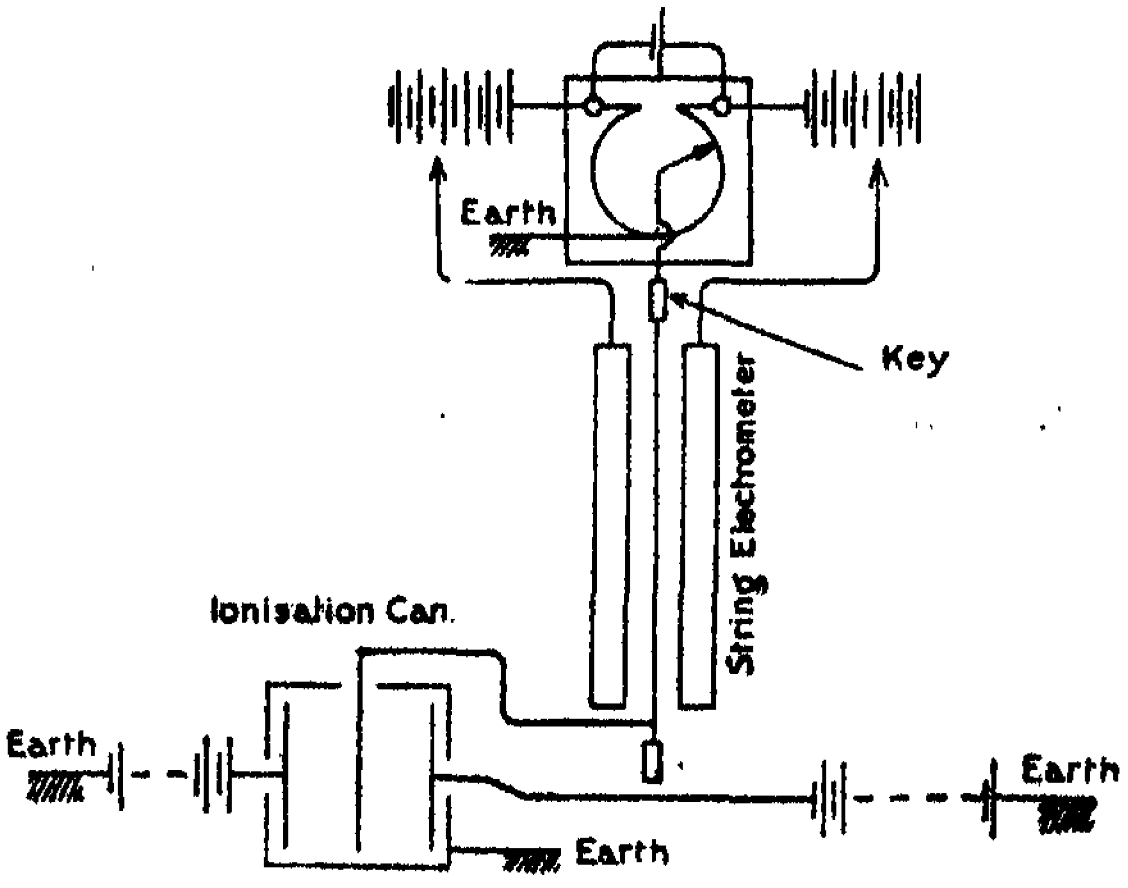

Fig. 5.

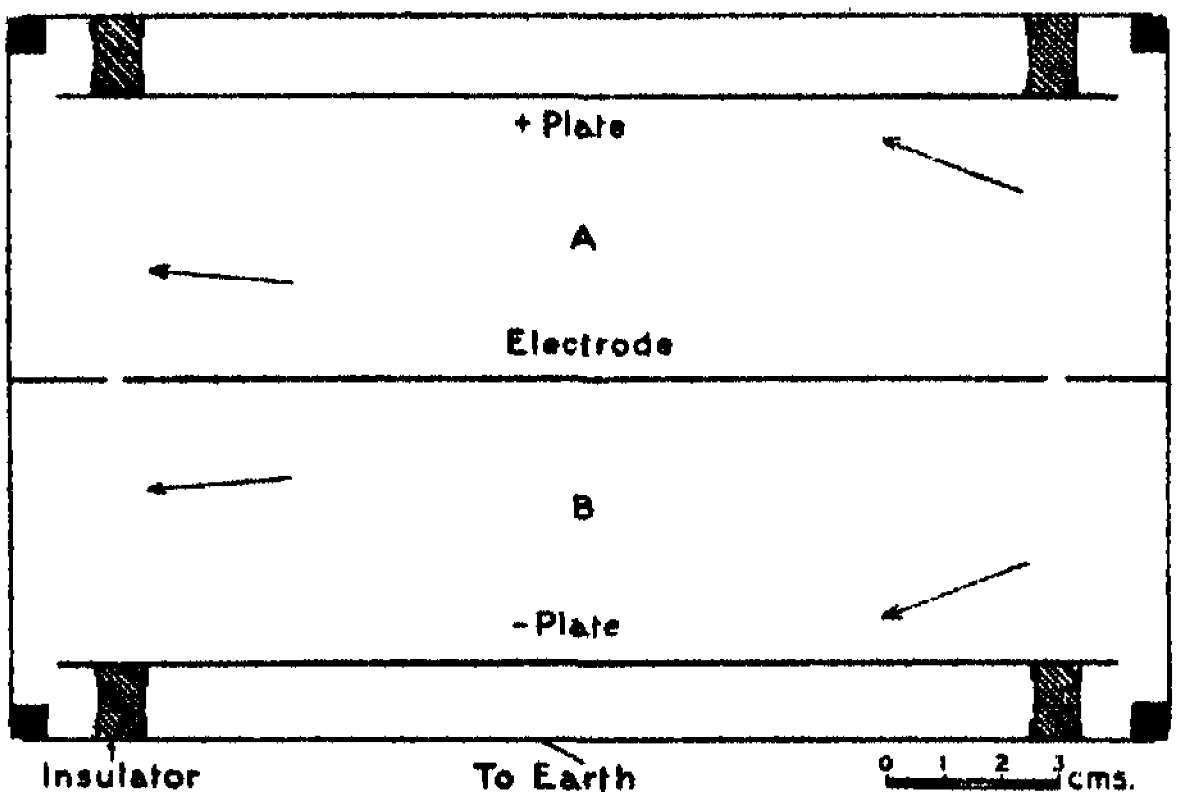

Fig. 6.

Fig. 1 shows the position of the radium with respect to the compartments of the ionisation can; fig. 4 the string electrometer, connected to the electrode of the double compartment ionisation vessel, and the camera for photographically recording the movement of the electrometer fibre; fig. 5 represents the electrical connections of the ionisation vessel and string electrometer; fig. 6 the details of the vessel. In the first experiments two exactly similar cylindrical cans were used, but subsequently these were abandoned for a single box-shaped vessel (figs. 1 and 6) divided into two compartments, A and B, by the electrode, the positive ions from A being collected by one side of the electrode and the negative ions from B by the other side; the excess of positive or negative electricity deflected the electrometer. The compartments A and B were made alike, and so the amount of ionisation in A due to the γ-rays was approximately equal to that in B, when the source of the γ-rays was in the plane of the electrode. A more exact balance could be readily obtained by slightly screening A or B, and so the electrometer fibre could be kept somewhere on the scale of an observing microscope, though its position was always fluctuating to a greater or less degree depending on the sensitiveness of the electrometer and other conditions.

The String Electrometer.—The string electrometer used in these experiments was designed by Mr. Horace Darwin and one of us.* In a previous paper† its characteristics have been described; the present instrument is the outcome of the experiments there described.

The general principle of the electrometer is very simple, a silvered quartz fibre taking the place of the gold leaf of the ordinary electroscope the variations from the usual forms of the latter instrument are that the fibre is fixed at both ends, is placed in a uniform field, and that the middle of it is observed with a high power microscope.

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* The electrometer was exhibited at the Royal Society Soirée in 1909.

† Laby, 'Proc. Camb. Phil. Soc.,' 1909, vol. 15, p. 106.

The string electrometer under notice has been found when once properly set up (which requires a good deal of care)* to be a reliable instrument which needs no attention and for which the sensitiveness is easily adjustable over a wide range. The fibre will follow rapid potential changes and the movements can be recorded photographically.

The electrometer is shown in fig. 7. The silvered quartz fibre of 15 cm. length is supported at one end by B, which is fixed when once the instrument is in adjustment, at the other end by a support on the lever E. These supports are such that the electrical insulation of the fibre is fused quartz.

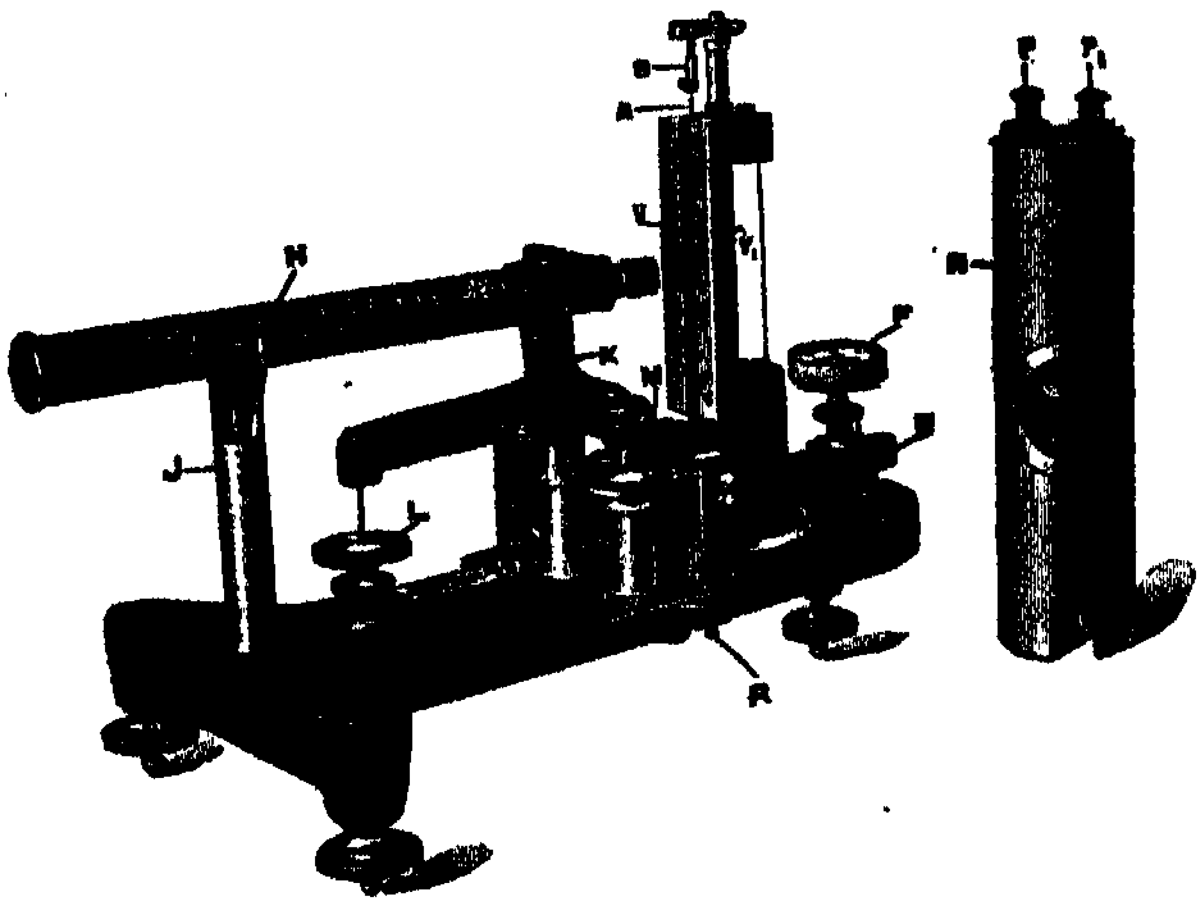

FIG. 7.

The distance between the supports and consequently the fibre tension is maintained by the invar plates V, V′, and so is subject to only small temperature variations. To obtain a fine and regular adjustment of the tension, one end of the lever E has knife-edges resting in geometrical V's, the other end is supported by the micrometer screw F carrying a graduated head. The fibre may be moved laterally by means of the screw G and its counterpart on the other side of the instrument, which slide the knife-edge of the lever E in its own direction. The quartz thread is stretched vertically between the plates V, V′, which are 1 cm. apart and are insulated. To establish the electric field which deflects the fibre these plates are put to a potential of $-V$ and $+V$, when the fibre is at zero potential.

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* The precautions required in setting up the string electrometer are similar to those required with the Wilson tilted electroscope; it is *essential* to shield the fibre from all air currents, for it is very sensitive to their action.

The motion of the middle of the fibre is observed with the microscope H, using a Zeiss C objective and a No. 3 micrometer eyepiece, a combination giving a visual magnification of 360 diameters. A higher magnification than this is usually less convenient. It will be clear from the figure how the microscope is supported, how the screw L focuses it, and the screw M moves it sideways. This focusing arrangement compares favourably with good microscope movements. It will be seen from the figure of the instrument that all necessary adjustments of the fibre and microscope can be readily made.

The fibre was illuminated by the light from a Nernst lamp (see fig. 4). The heat rays were removed by the cell B, which contained a saturated ferrous ammonium sulphate solution; the remaining rays passed through a condenser and came to a focus on the fibre, which, illuminated in this way, appeared black on a bright ground. A camera shutter for cutting off the light enabled time signals to be recorded on the film.

Sensitiveness.—How the factors (1) distance of the plates apart, (2) their potential difference, (3) the tension of the fibre, affect the sensitiveness of the string electrometer has been considered in the paper previously mentioned. When the electrometer as re-designed was first tested, the potential difference between the plates used was from 40 to 100 volts, but though the high sensitiveness of from 1000 to 1500 eyepiece divisions* per volt could be obtained it was found better to work with a P.D. of from 4 to 12 volts, as the sensitiveness remained steadier and could be conveniently used at over 500 divisions per volt. The sensitiveness can be readily adjusted to a desired value by altering the plate P.D., the tension of the fibre, or the magnification of the microscope; generally an alteration in the P.D. is all that is necessary. For a sensitiveness up to 700 divisions per volt the zero is very steady; beyond this it is subject to slight slow changes. The instrument was designed for recording the fluctuations in voltage such as arise in the investigations of the type initiated by von Schweidler. A few rough tests were made with the electrometer when it was first set up to find how rapidly the fibre would take up a new position when its potential was changed. In these tests the tension on the fibre was increased to alter the sensitiveness, and the P.D. of the plates was kept constant at 100 volts. The following table contains the results obtained :—

Magnification 360.

Sensitiveness in eyepiece divisions.	Percentage of full deflection.	Time required.
	per cent.	sec.
130	50	0·3
40	50	0·17
15	66	0·08

Screening.—In the experiments recorded below, the electrometer was screened from the γ-radiation by a heavy lead screen, L-shaped in section and 2·3 cm. in thickness (*shown dotted in side view in fig.* 4). The effect of the radium on the screened electrometer was deduced, from experiments with additional screens, to be negligible. With the original form of apparatus attempts were made to obtain a definite beam of γ-rays through the two cans by using for each a protecting lead cylinder, 4·5 cm. thick, with a central hole, also by inserting the radium in a lead cylinder, 9 cm. in diameter, with a narrow lateral hole. The definition of the beam thus obtained was not, however, sufficiently good to justify the method.

The Ionisation Vessel.—This vessel was designed (1) to make the whole apparatus as sensitive as possible to fluctuations in the ionisation; (2) to give a uniform electric field of such intensity, using the battery power available, that the ionisation current would be saturated. The second of these conditions implies a parallel plate condenser for the ionisation vessel.

The following considerations are of importance in the design of the ionisation vessel:—Let C be the capacity of the electrode, c that of the electrometer, insulators, and connections, n_1v_1 and n_2v_2 the number of pairs of ions formed during unit time in the effective volumes v_1 and v_2 of air on the opposite sides of the electrode, E the rate of rise of the potential of the electrode and fibre due to the excess of ions generated on one side. If A is the area of the electrode, and d its distance from the plates, then $v_1 = v_2 = v = Ad$.

The rate of deflection of the fibre is

$$D = \lambda E = \lambda ev(n_1 - n_2)/(C+c) = \lambda'\left(\frac{C}{v}+\frac{c}{v}\right)^{-1} = \lambda'\left(\frac{1}{4\pi d^2}+\frac{c}{v}\right)^{-1},$$

where λ′ is independent of the dimensions of the can.

For D to be large, d and v/c or Ad/c must be large, *i.e.* the capacity of the connections and electrometer should be small, and the distance between the plates large. The first vessels made were cylindrical with two electrodes, each parallel to the plane ends; for each can $v = 56$ c.c., $c = 1·1$ cm. E.S.U., $d = 2$ cm.; for the whole system $C = 33$ cm. E.S.U., or 15 times as much as the electrodes. This large capacity, which was mostly in the four guard-ring insulators and connections, was surprisingly large and made the apparatus insensitive. The distance between the plates had been made small, in order that when using methyl bromide or methyl iodide in the vessels, it would be possible with the available voltage to saturate the ionisation currents for the intensities used. It was found, however, that the ionisation in these vapours was so little greater than that in air as to make their use of no advantage. For example, saturating the air with methyl iodide increased the ionisation about 1·7 times. It was decided to re-design the ionisation vessel, so as to increase the distance between the electrode and the plates, and to use only one insulator so as to make the capacity of this portion a minimum. The increase in d was possible, as Mr. Lattey* and Prof. Townsend find that the very perfect drying of air increases the mobility of ions, from which it would follow that a given ionisation in air dried by phosphorus pentoxide could be saturated with a smaller field than the same ionisation in moist air. As re-designed, the vessel is as shown in fig. 6. Its dimensions are: Plate distance 4·85 cm., capacity of electrode (C) 6·6 cm., effective volume (v) 1950 c.c., and v/c 295 c.c. per centimetre of condenser capacity compared with 50 for the first vessel. On the above theory the fluctuations in the deflection of the fibre with the radium at a given distance should be greater in the case of the second apparatus than in that of the first; this was verified in the experimental work, the increase being quite distinct.

The Batteries.—Since the object of these experiments was to detect the presence or absence of fluctuations under particular circumstances, very steady sources of potential were needed. The steadiness of the voltage of the small accumulators used (supplied by W. G. Pye, Cambridge) was therefore tested, 60 cells at a time being connected to a Kelvin electrostatic voltmeter, which was read with a microscope. The final observations were made with the voltmeter floating in a vessel of mercury, supported on a brick pillar to eliminate vibrations. The changes in the voltage of the cells were found to be not more than 0·01 volt per 120 volts, *i.e.* 0·01 per cent., the time of observation ranging up to 18 minutes. From the character of the curves obtained, it seemed probable that many of the variations found were in reality produced by earth tremors. The steadiness of the fibre (as shown photographically), when connected to the electrode, and so exposed to any induction effects from the potential plates, confirmed the previous experiments. To obtain such constancy, the mercury connections had to be most carefully amalgamated.

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* 'Roy. Soc. Proc.,' July, 1910, A, vol. 84, p. 173.

Observation of Fluctuations.

In taking observations, the main initial adjustments comprised the testing of the insulation of the fibre, and the determination and adjustment of the sensitiveness. In the first experiment, records were taken of the movement of the fibre by plotting readings on the eyepiece scale against a time co-ordinate. The first set of readings was taken with the conditions exactly similar to those under which the radium was to be present later, the connection of the fibre system to earth being broken. Then the radium was brought into position, and the currents in the two compartments of the ionisation vessel adjusted as nearly as possible to equality by partially screening one of the compartments (or, in the original apparatus, one of the cans). Readings were then again taken over a given time. Finally, a third set was taken with the radium removed, and the fibre again free. The absence of fluctuation in the first and last cases eliminated the possibility of spurious effects. The chief causes of these latter were draughts in the electrometer, faulty connections and cells. In some of the final results, all observable effects due to these causes were eliminated.

The original form of apparatus was sufficiently good to show fluctuations in the ionisation due to γ-rays from the radium, but the form now in use shows these more distinctly. Fig. 8 was obtained by one observer plotting the position of the fibre, as called by the other observer, every 5 seconds.

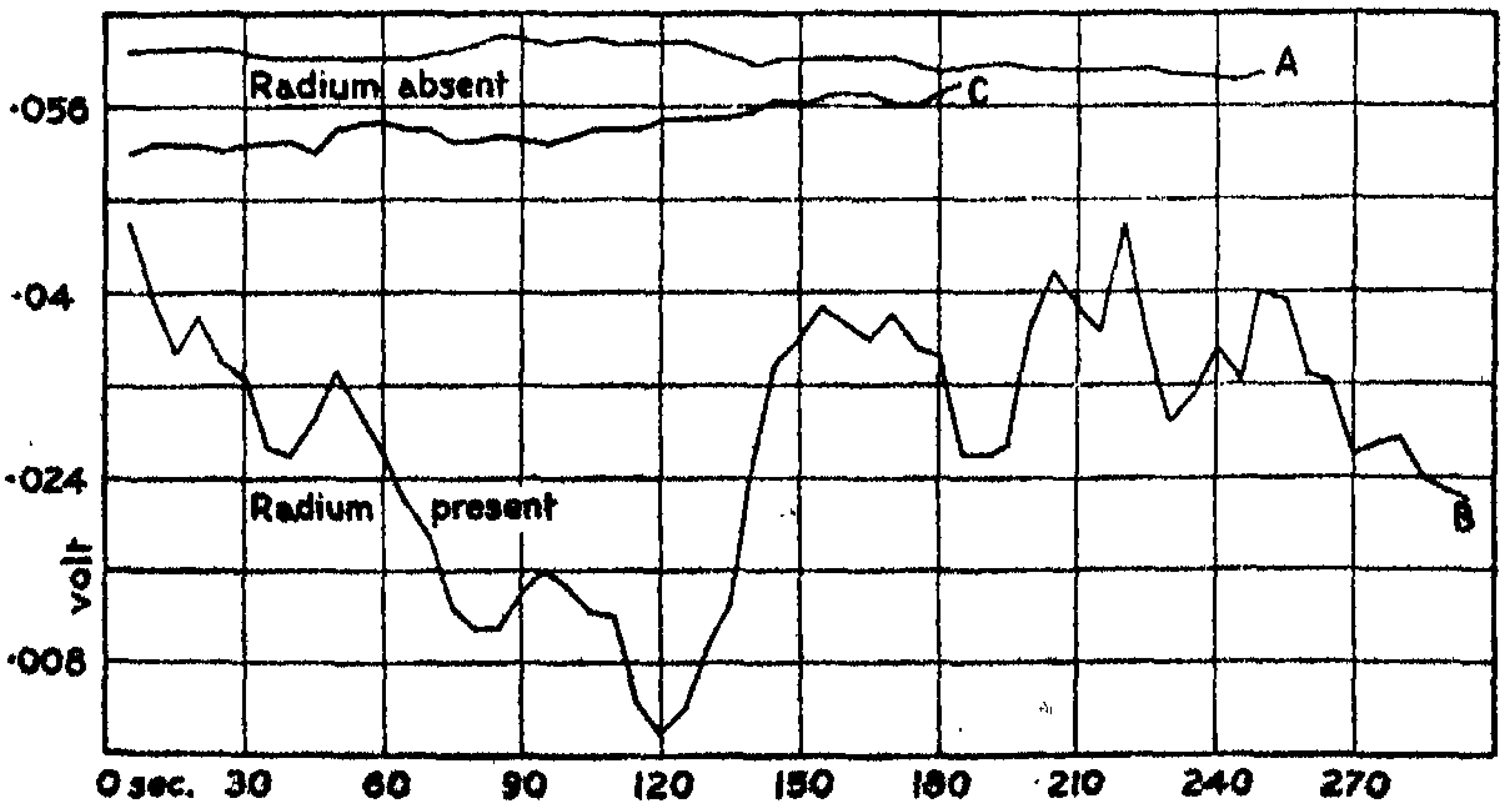

Fig. 8.

In later experiments the movements of the fibre were photographically recorded; a Kodak camera was fitted to the end of the microscope, and an adjustable slit in a brass screen allowed a small portion of the image of the fibre to fall on the film. The latter was wound past the slit by a winding gear, fitted to the ordinary winder on the camera, and driven by a small electric motor. The initial tests and adjustments were made by observing the image on a ground-glass plate. The ionisation currents in the can were balanced at the start, the radium held in an adjustable arm being symmetrically placed (see fig. 1) with respect to the two compartments. The radium could be removed and inserted again in approximately the same position. Time signals on the sensitive film at each operation were made with the shutter on the Nernst lamp. The process consisted in obtaining a record of the position of the fibre in the following order:—

Fibre earthed.
„ free for some minutes with radium present.
„ earthed.
„ free for some minutes with no radium present.
„ earthed.

The graph A of fig. 8 represents the movement of the fibre during 3 minutes 45 seconds with no radium present, and so shows any spurious fluctuations (produced by draughts, mechanical tremors, variations in the E.M.F. of the batteries in use, and in the natural ionisation) which existed immediately before the graph C was obtained; the graph C represents the disturbances due to the same causes existing immediately after the curve B was taken; and B represents the fluctuations during 5 minutes when the radium was present. There can be little doubt that these graphs show that the ionisation produced by γ-rays in air fluctuates.

In fig. 9 are shown two films (curves I and II) on which the position of the fibre was continuously photographed. In curve II, for which the electrometer was very sensitive, giving 1000 eyepiece divisions per volt, γ-rays from the radium were acting during the time from S to T; the fluctuations are clearly shown. From T to U the radium was absent and the fluctuations disappear, although the fibre drifts a little. Curve I gives a similar record; the greater steadiness of the fibre when the radium was absent is due to the lower sensitiveness used—400 divisions per volt, though this particular film is one of the least favourable in this respect. Here, again, from A to B the radium was present, and from B to C absent, the conditions otherwise, when the fibre was free, being exactly similar. The effect of distance of the source of rays is also qualitatively shown by the two curves—I is taken with the radium 20·4 cm. from the front of the ionisation vessel, II with the radium only 5·8 cm. away. The extent of the fluctuations, when both are reduced to the same scale, is much diminished with increased distance—a result to be expected from the decrease in the intensity of ionisation.

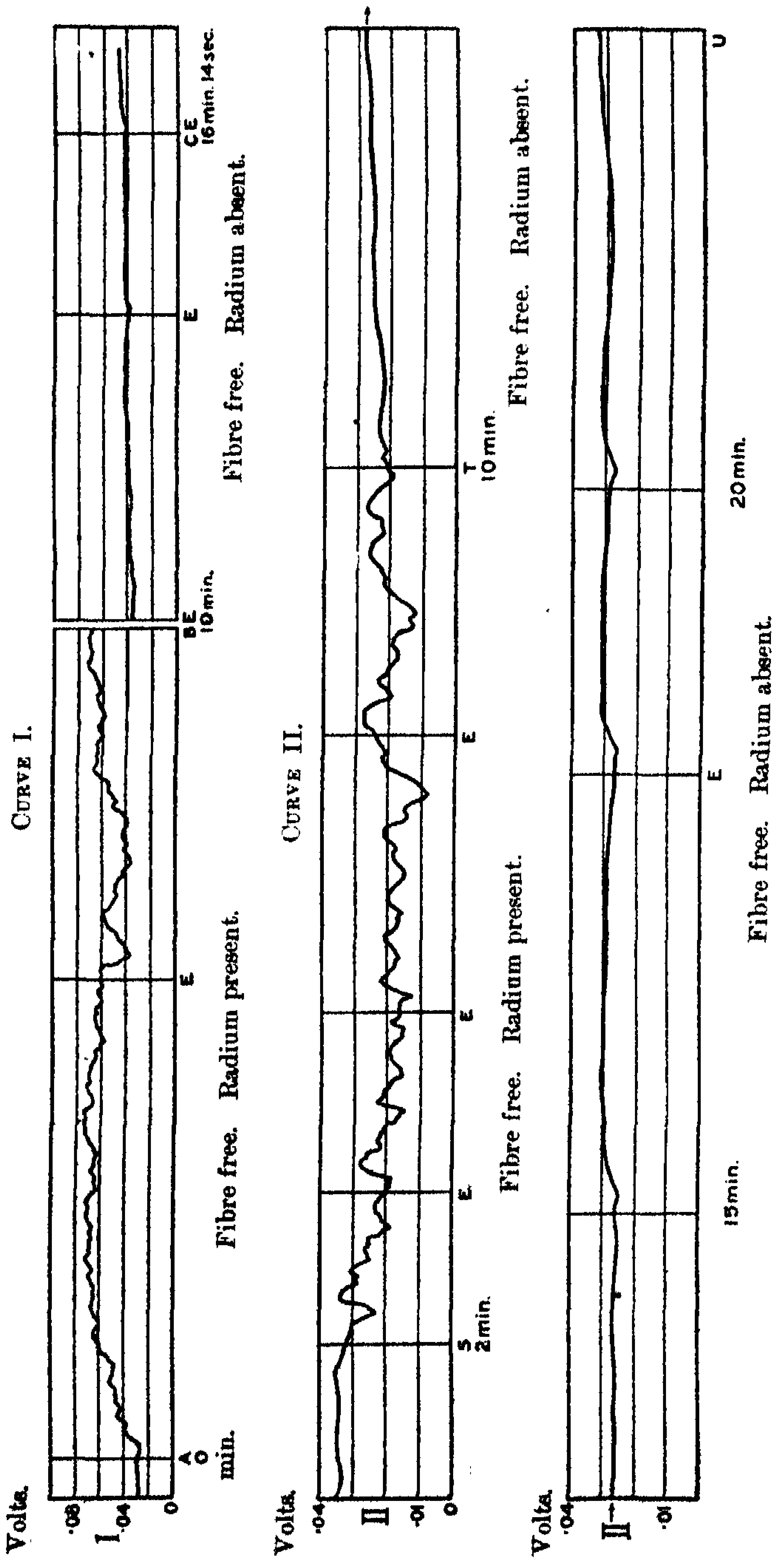

Fig. 9.—Curve I, radium at 20·4 cm. distance; Curve II, radium at 5·8 cm. distance. E = earthed.

The break in curve I at B is due to the fact that the shutter on the Nernst lamp was inadvertently left closed after the signal immediately preceding the earthing of the fibre and removal of the radium.

We think that these records, which are only two of many similar, fully demonstrate the existence of fluctuations in the ionisation produced by γ-rays. By using a string electrometer, which is capable of following more rapidly the changes in voltage of the electrode than a quadrant electrometer, the time necessary to complete an experiment has been reduced; further, we have avoided the use of a Bronson resistance, and any possibility of the introduction of variations by it.

As we have already seen, the fluctuations may be due to the action of two factors—(1) a relative fluctuation in the number of γ-rays entering the two compartments of the ionisation vessels used, and (2) a fluctuation in the number of ions generated in the vessel per γ-ray. It will be necessary to make further experiments to determine the part which these two factors play. If Prof. Bragg's view of the process of ionisation by γ-rays is correct, then the fluctuations we have observed would be almost entirely due to the second factor, and they would not be a proof of the projected entity (corpuscular) theory of γ-rays.

If, on the other hand, Meyer's results with CO_2 and air are correct, then the number of ions generated by a γ-ray is constant, and our results are evidence of the projected entity (corpuscular) nature of γ-rays. We believe that with the apparatus we are using, *i.e.* the double compartment ionisation vessel and the photographically recording string electrometer, it will be possible to obtain a solution of these questions.

These experiments were begun in the Cavendish Laboratory, Cambridge, continued in the Physical Laboratory of the University of Sydney, and completed in Wellington. To Sir J. J. Thomson and Prof. Pollock we are indebted for encouragement and help. The Royal Society rendered the completion of the experiments possible by the loan of the 5 mgrm. radium bromide we have used.

We have to thank Dr. G. W. C. Kaye and Mr. N. R. Campbell for looking through the proofs of this paper.

On the Velocities of Ions in Dried Gases.

By Robert Tabor Lattey, M.A., Trinity College, Oxford, and Henry Thomas Tizard, M.A., Fellow of Oriel College, Oxford.

(Communicated by Prof. J. S. Townsend, F.R.S. Received January 20,—Read February 22, 1912.)

An account was recently given of a method by which the velocities of both positive and negative ions produced by Röntgen rays could be measured in very dry gases,* and some measurements were given for ions in air. These measurements have now been extended to the cases of carbon dioxide and hydrogen, and some calculations, based on the work of Townsend,† show that, while the positive ions retain a large envelope of matter even under the influence of a fairly large field of force, the negative ions become considerably diminished in size when their velocity is increased either by an increased force or by diminished pressure.

While these results are in general accord with those of other observers, yet the point which has hitherto escaped notice is that the negative ions are far more readily deprived of their customary envelope in a very dry gas than in a comparatively moist atmosphere.

In the paper already cited it was shown that the velocity of ions in air is a function of X/p, where X is the potential gradient, and p the pressure of air in the apparatus, and that this function is independent of the actual values of either X or p, but is considerably affected by minute traces of moisture. This result has been confirmed for ions in hydrogen and in carbon dioxide, and evidence has been obtained that the velocities of negative ions in air are affected by traces of carbon dioxide, while those in hydrogen are considerably lowered by traces of air.

These facts may be compared with the observations of Franck and Pohl,‡ who have shown that the velocities of negative ions in nitrogen and argon are very considerably lowered by moisture and other impurities. Unfortunately these workers used Rutherford's method of estimating the mobilities of ions, and this involves the use of an alternating E.M.F. which is a sine function of the time. As our experiments have shown that the velocity of a negative ion is not a linear function of X (at constant pressure), it is impossible to deduce true values of the ionic velocities from Franck and Pohl's observations.

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* R. T. Lattey, 'Roy. Soc. Proc.,' 1910, A, vol. 84, p. 173.

† 'Phil. Trans.,' 1900, A, vol. 193, p. 139; 'Roy. Soc. Proc.,' 1908, A, vol. 81, p. 464; 1911, A, vol. 85, p. 25.

‡ 'Ber. der Deutsch. Phys. Ges.,' 1907, pp. 69, 194; 1909, p. 397; 1910, pp. 213, 291.

Apparatus.—The apparatus used was the same as that described in the paper quoted above, with the exception that the soda lime tube (H, p. 175) was removed before carbon dioxide was admitted.

It was found to be far more difficult to dry an apparatus containing carbon dioxide than one containing other gases; this is probably owing to slowness of diffusion. In the experiments with hydrogen it was found necessary always to use freshly prepared gas, especially at low pressures, since gas which had been in the apparatus some days gave inconsistent results, presumably owing to the infiltration of minute traces of air, or to small quantities of other gases from the grease of stopcocks and similar sources.

Results.

(1) *Positive Ions.*—As in the case of air, it was found that the velocities of positive ions in carbon dioxide were proportional to X/p over the range of forces and pressures that were used. The velocities of positive ions in dried hydrogen appear from our results to increase slightly with X/p. The results are shown in the following tables:—

Table I.—Velocities of Positive Ions in Dried Hydrogen.

No.*		p (mm.).	X (volts per cm.).	X/p.	v (cm. per sec.).	vp/X.
1	H. T. T.	72·0	2·71	0·0376	140	3730
2	R. T. L.	54·9	1·93	0·0352	135	3860
3	,,	54·9	2·26	0·0411	159·5	3880
4	,,	46·6	2·26	0·0485	192	3960
5	,,	40·0	2·24	0·0560	208	3710
6	H. T. T.	36·0	2·51	0·070	257	3780
7	R. T. L.	34·3	2·24	0·0654	289	4410
8	H. T. T.	29·1	2·69	0·092	360	3910
9	,,	29·1	2·34	0·080	320	3980
10	,,	21·5	2·04	0·095	385	4070
11	,,	19·7	2·00	0·101	441	4340
12	,,	10·0	2·03	0·203	850	4180
13	,,	5·35	1·13	0·211	1020	4950
					Mean.........	4058

* Initials indicate the observer responsible for the experiment.

Table II.—Velocities of Positive Ions in Dried Carbon Dioxide.

No.		p.	X.	X/p.	v.	vp/X.
1	R. T. L.	12·9	2·86	0·222	139	626
2	,,	12·9	2·92	0·226	148	655
3	,,	13·7	2·62	0·191	117·8	616
4	,,	11·5	2·62	0·227	150·5	663
5	,,	6·7	1·26	0·188	118·5	630
6	,,	6·7	1·54	0·227	144	635
7	,,	6·7	1·815	0·271	187·5	691
8	,,	6·7	2·07	0·309	205	664
9	,,	6·7	2·36	0·352	226	641
10	H. T. T.	5·53	2·26	0·409	255	623
11	,,	3·68	1·06	0·451	295	654
12	,,	3·68	1·94	0·527	344	653
13	,,	3·68	2·24	0·609	361	593
					Mean.........	642

Table III.—Velocities of Positive Ions in Moist Carbon Dioxide. (H. T. T.)

No.	p.	X.	X/p.	v.	vp/X.
1	7·56	2·14	0·283	175	618
2	7·0	2·30	0·329	200	609
3	6·47	2·23	0·345	208	624
4	5·28	2·09	0·396	235	596
5	3·71	1·66	0·447	284	635
				Mean	616

The following table contains the values of vp/X obtained by other observers :—

Observers.	Air.		CO$_2$.		H$_2$.	
	Dry.	Moist.	Dry.	Moist.	Dry.	Moist.
L. and T.	1121	780	642	616	4058	
Langevin	1100	—	—	654		
Zeleny	1040	1030	578	622	5090	4030
Wellisch	1170	—	—	616		
Chattock	1071	996	—	631	—	4105
Chattock and Tyndall	—	—	—	—	—	4310
Phillips	—	1060				
Przibram	908	841				
Franck and Pohl	1360	1004				
Blanc	965	1130	630	667	—	4050

It may be mentioned that Zeleny's and Blanc's observation, that positive ions travel faster in moist than in dry carbon dioxide, could not be confirmed.

(2) *Negative Ions.*—As in the case of air, it was found that the velocity of negative ions in dried carbon dioxide and in dried hydrogen increases more rapidly than X/*p*, as is shown by the following tables of results :—

Velocities of Negative Ions in Carbon Dioxide. Series *a*. Imperfectly Dried. (R. T. L.)

No.	*p*.	X.	X/*p*.	*v*.
1	32·2	2·60	0·0807	73·7
2	32·2	2·92	0·0905	74·2
3	27·8	2·59	0·093	83
4	27·8	2·89	0·1075	87·3
5	24·6	2·58	0·105	86·3
6	24·6	2·92	0·1185	99·7
7	19·4	2·92	0·150	122·5
8	16·2	2·54	0·157	147
9	16·2	2·86	0·1765	159
10	15·3	1·74	0·114	103
11	15·3	2·01	0·131	127·5
12	15·3	2·83	0·185	174
13	11·55	1·73	0·150	138
14	11·55	2·00	0·173	157·5
15	9·9	1·035	0·105	87

Further observations showed that the value of *v* corresponding to any particular value of X/*p* was increasing as the moisture was being absorbed, and a week later the following results were obtained :—

Series *b*.

No.	*p*.	X.	X/*p*.	*v*.
1	11·25	1·78	0·158	368
2	9·2	2·20	0·239	2800 +
3	8·9	1·10	0·1235	145
4	8·9	1·36	0·1525	235·5
5	6·7	0·90	0·134	118·5
6	5·81	0·585	0·101	97
7	5·81	1·17	0·202	2000
8	5·85	1·43	0·245	9000

A fresh quantity of CO_2 was then admitted, and another set of measurements were made (Series *c*). Between Series *c* and *d*, and also between *d* and *e*, the apparatus was exhausted and refilled with gas which had stood for some days in contact with phosphorus pentoxide.

Series *c*, *d*, and *e*.

No.	*p*.	X.	X/*p*.	*v*.
1*c*	19·2	2·57	0·134	122
2*c*	18·4	2·30	0·127	122
3*c*	18·4	2·59	0·141	159
4*c*	16·6	2·30	0·138	162
5*c*	15·0	2·30	0·153	344
1*d*	15·9	2·54	0·160	418
2*d*	15·1	2·56	0·169	1270
3*d*	15·74	1·99	0·126	117
4*d*	15·74	2·30	0·146	192
5*d*	15·74	2·30	0·146	234
6*d*	15·74	2·56	0·162	539
7*d*	14·0	1·99	0·142	197·5
8*d*	14·0	2·27	0·162	500
9*d*	14·3	2·56	0·179	1435
10*d*	13·1	1·715	0·131	135
11*d*	13·1	2·015	0·154	354
12*d*	13·0	2·20	0·1735	1270
1*e*	13·4	1·14	0·0855	70
2*e*	12·0	1·16	0·0965	102
3*e*	11·35	1·44	0·127	150
4*e*	11·35	1·70	0·150	297

Velocities of Negative Ions in Dried Hydrogen. Series *a*. Imperfectly Dried.

No.	*p*.	X.	X/*p*.	*v*.	*vp*/X.
1	160·0	2·39	0·0149	89·2	5987
2	150·0	2·39	0·0159	98·4	6189
3	135·2	2·39	0·01695	106·7	6295
4	135·2	2·09	0·01545	97·2	6292
5	135·2	2·60	0·0192	129·6	6750
6	135·2	2·97	0·0220	165·0	7500
7	124·5	2·34	0·0188	122·5	6516
8	124·5	2·63	0·0211	138	6540
9	124·5	2·64	0·0212	146	6886
10	124·5	2·92	0·02345	153	6525
11	106·8	2·04	0·0191	125	6544
12	106·8	2·60	0·02435	165	6776
13	94·0	2·03	0·0216	135	6250
14	93·1	2·34	0·0252	170	6746
15	93·1	2·60	0·0279	194·2	6960

These results were obtained with the first filling of gas, after washing out the apparatus several times, and are possibly affected by minute traces of CO_2. They are given here to show the extraordinary effect of small traces of impurity—less than 1 in 1000 probably. The following results were obtained with several different samples of dried hydrogen:—

No.	p.	X.	X/p.	v.
1	197·6	2·57	0·0130	102
2	171·8	2·29	0·0133	104·5
3	171·8	2·57	0·0150	149
4	171·8	2·58	0·0151	141
5	154·2	2·29	0·0148	138
6	154·2	2·57	0·01665	180
7	92·2	2·00	0·0217	500
8	92·2	2·56	0·0278	1475
9	90·6	1·44	0·0159	119
10	90·6	1·745	0·0193	380
11	82·5	1·44	0·0175	141
12	82·5	2·57	0·0311	2080
13	73·6	0·83	0·0113	84·3
14	73·6	1·69	0·0229	475
15	73·2	1·10	0·0150	170
16	73·2	1·415	0·0193	310
17	67·6	1·415	0·0209	445
18	67·6	1·43	0·0211	451
19	67·6	1·44	0·0214	406
20	67·6	1·715	0·0253	1019
21	67·6	1·74	0·0259	1141
22	67·3	1·69	0·0251	825
23	66·9	0·83	0·0124	114
24	66·9	1·13	0·0169	220

All these results are shown graphically in figs. 1 and 2. It will be seen that the curves all have the same general shape. The following tables, which have been compiled from the mean curves, show the velocities corresponding to various values of X/p:—

Carbon Dioxide—

X/p	0·08	0·09	0·10	0·11	0·12	0·13	0·14	0·15	0·16	0·17
v	64	73	82	92	106	132	182·5	277	468	977

Hydrogen—

X/p	0·010	0·012	0·014	0·016	0·018	0·020	0·022	0·024	0·026	0·027
v	68	95	127	174	236	336	489	730	1100	1347

In all cases, the velocities for comparatively small values of X/p approximate to a linear function of that quantity. The values of vp/X for these small values of X/p may be compared with those obtained by other observers:—

Observers.	H_2.		CO_2.	
	Moist.	Dry.	Moist.	Dry.
L. and T.	—	6170	—	800
Zeleny	4255	6040	570	615
Rutherford	2965	—	598	—
Kovarik	—	—	612	770
Wellisch	—	—	624	—
Langevin	—	—	683	—
Blanc	—	7600	644	783
Chattock	—	5650	703	—
Chattock and Tyndall	—	5455	—	—

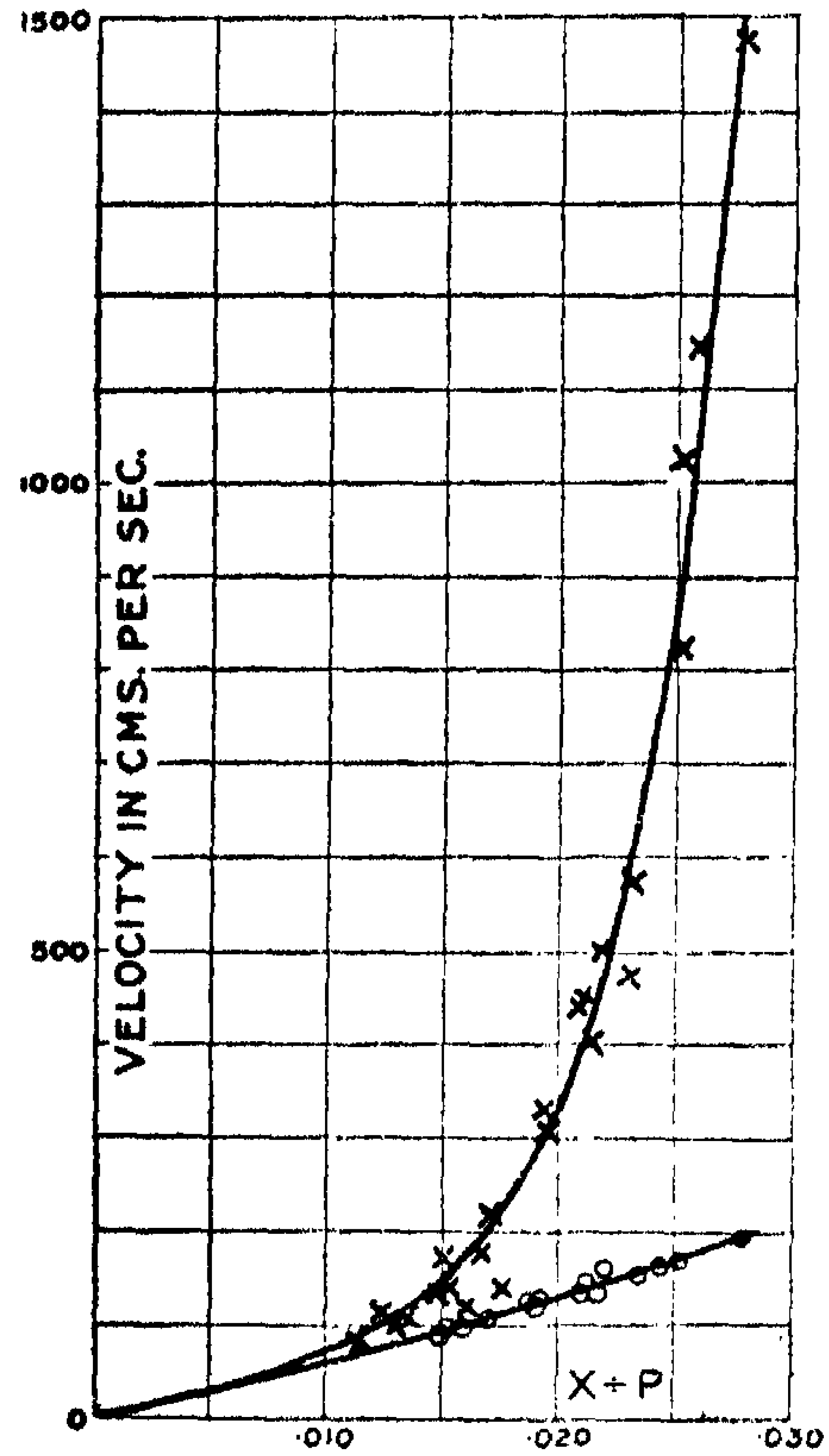

FIG. 1.—Hydrogen.

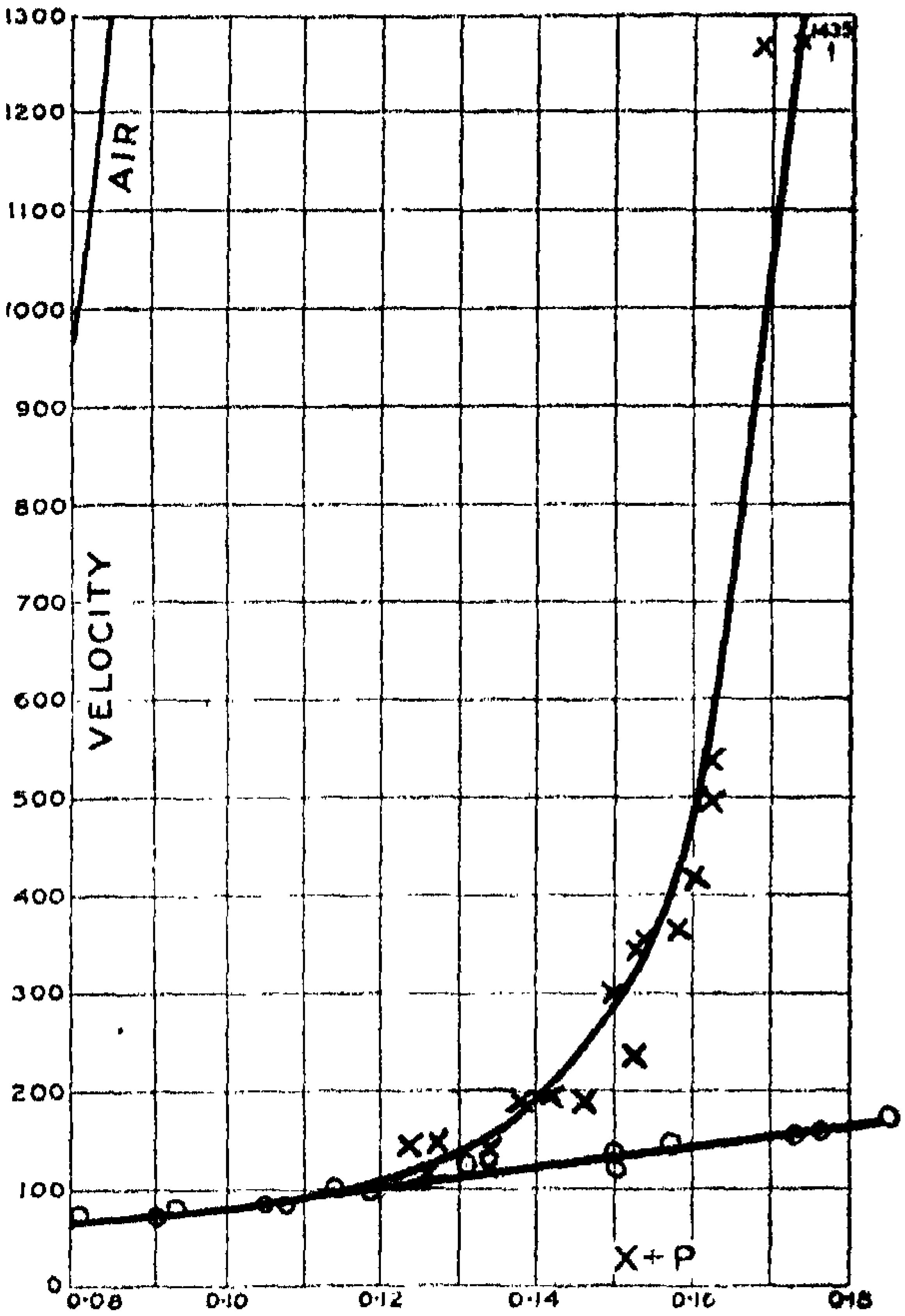

FIG. 2.—Carbon dioxide.

× dry. o moist.

Discussion of Results.

Since the positive ions show a linear relationship between v and X/p, the ordinary formula

$$D = \frac{\Pi v'}{NeX}, \quad \text{or} \quad D = 3{\cdot}21 \times 10^{-5}\frac{vp}{X}$$

may be applied, where D is the diffusion coefficient between the ions and the gas in which they are moving with velocity v' at atmospheric pressure (Π).* From this, an approximate value for the molecular masses of the ions may be obtained by using the formula $D^2 m_1 m_2 = K^2$; m_1 and m_2 being the molecular masses of the gases between which diffusion is taking place, and K being a constant. Comparison of the available data for gases gives an average value for K of about 4·6, when the molecular masses are in the ordinary chemical units.

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* Townsend, 'Phil. Trans.,' 1900, A, vol. 193, p. 129.

	vp/X.	D.	m.
Air	1121	0·0360	564
CO_2	642	0·0206	1144
Hydrogen	4058	0·1303	624

It appears therefore that the positive ion has a large mass, and is probably an aggregate of at least 25 molecules of the gas in which it is formed, clustered round an electronic nucleus.

In moist gases, and in dried gases with small values of X/p, a similar calculation can be made, but with higher values of X/p the velocities are not linear functions of this ratio. But Townsend has shown that to obtain the true values of D in these cases, the quantity $\Pi v'/NeX$ must be multiplied by $\sqrt{k}$, where k is a factor which can be deduced from his experiments on the lateral diffusion of a narrow stream of ions in an electric field of force.* The complete equation for determining the molecular mass of a negative ion thus becomes

$$m = \frac{K^2 (NeX)^2}{k (\Pi v')^2 m_1}.$$

Unfortunately, it is only in the case of air that any values of k are given. In the case of other gases it is only possible to give calculations of mk, where k may have any value greater than unity, but probably less than 10.

Air.

X/p.	vp/X.	D.	k.	m.
0·04	2812	0·1009	1·25	72
0·05	3462	0·1295	1·36	43·5
0·06	4797	0·1875	1·48	21
0·07	7293	0·2950	1·59	8·5
0·08	11920	0·5005	1·71	2·5
0·09	20500	0·890	1·83	0·9

CO_2. Hydrogen.

X/p.	vp/X.	$Dk^{-\frac{1}{2}}$.	mk.	X/p.	vp/X.	$Dk^{-\frac{1}{2}}$.	mk.
0·08	800	0·0257	725	0·010	6800	0·2183	221
0·09	810	0·0260	708	0·012	7917	0·2541	168
0·10	820	0·0263	692	0·014	9070	0·2912	124
0·11	836	$0·0268_5$	664	0·016	10875	0·3491	86·5
0·12	883	$0·0283_5$	596	0·018	13110	0·421	59·5
0·13	1015	0·0326	450	0·020	16800	0·539	36
0·14	1304	$0·0418_5$	273	0·022	22230	0·7135	21
0·15	1847	0·0593	136	0·024	30420	0·976	11
0·16	2925	0·0939	54	0·026	42310	1·358	6
0·17	5747	0·1845	14·5	0·027	49880	1·601	4

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* 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 28.

It would appear, therefore, that a negative ion in a dried gas has, like a positive ion, an envelope of molecules about its electronic nucleus, and that when a certain velocity is exceeded the electron is partially deprived of this envelope by its collision with the molecules of the gas. This will increase its mobility in two ways: (1) on account of the decreased mass of the ion its acceleration between impacts will be increased; (2) its decreased radius will give it a greater freedom from collisions.

The values given above for the molecular mass must, therefore, be regarded as the average value of the mass of the group of molecules associated with the electron. Since this mass becomes smaller than that of an air or CO_2 molecule—and probably also than that of a hydrogen molecule—it is clear that in these gases the electron must have free existence during some part of its course.

The envelope of an electron may consist of water molecules or of molecules of the gas in which it is moving. This research has shown that with increasing velocities this envelope is more easily removed the fewer the water molecules present, and it would appear, therefore, probable that the envelope in dry gases consists of molecules of the gas, and that these are more easily removed than water molecules.

The researches of other investigators have shown that the negative ion appears to retain its envelope more persistently in an impure than in a pure gas, and their results may be compared with those given here.

Pure gas.	Impurity.	Authority.
Nitrogen	Oxygen	Franck, 'Ber. der deutsch. phys. Ges.,' 1910, p. 618.
"	Chlorine	
"	Water	
Argon	Oxygen	Franck, 'Ber. der deutsch. phys. Ges.,' 1910, p. 291.
Hydrogen	"	Chattock and Tyndall, 'Phil. Mag.' 1910, vol. 19 [6], p. 449.
Air	Water	R. T. Lattey, 'Roy. Soc. Proc.,' A, 1910, vol. 84, p. 173.
Carbon dioxide	"	R. T. L. and H. T. T.
Hydrogen	"	

Short Index to Reports of Physical Observations (Electric, Magnetic, Meteorological, Seismological) made at Kew Observatory.

Communicated by Dr. C. CHREE, F.R.S., by request of the Gassiot Committee.

(Received January 25,—Read February 22, 1912.)

A summary of observational data obtained at Kew Observatory used to be given in an Annual Report, which was printed in the Royal Society's 'Proceedings' up to the year 1900. From 1901 to 1909 these data were published in the Annual Report of the National Physical Laboratory, of which Kew Observatory then formed a department. The data for 1910 have been published by the Meteorological Office, which came into occupation of the Observatory on July 1, 1910.

As the Reports of the National Physical Laboratory are not unlikely to be overlooked by those whose primary interest is in observational work, the Gassiot Committee decided, in October, 1911, that it was desirable that a short list of their observational contents should be published in the Royal Society's 'Proceedings.' The descriptions of the data, which appeared in tabular form in the Annual Reports, are arranged below according to the subject; when there is no specific statement to the contrary, they refer to Kew Observatory. References to some of the more outstanding phenomena —especially the magnetic storms—will be found in the text of the Annual Reports.

Electrical.

Mean hourly values of the absolute potential of the Kelvin "water-dropper" for each month, from 10 quiet days, and, based thereon, mean diurnal inequalities of the potential gradient in the open for the 12 months, three seasons, and the year.

In 1907, 1908, and 1909 mean monthly values of "dissipation" of positive and negative electrical charges obtained with an Elster and Geitel apparatus.

Magnetic.

Mean hourly values of declination and horizontal force for each month, from the Astronomer Royal's "quiet" days, and diurnal inequalities deduced from these hourly means for two seasons ("summer" and "winter") and the year.

Mean monthly values of inclination and vertical force.

Mean annual values of declination, inclination, horizontal force, and vertical force, from all observatories contributing these data to the Kew Observatory.

In 1901 and 1903, mean hourly values of Falmouth declination and horizontal force, from the Astronomer Royal's "quiet" days, for 1901, 1902, and 1903—the latter two years in the 1903 volume—and diurnal inequalities (analogous to the Kew ones) based thereon.

For the same three years particulars of the Falmouth dip observations, and mean monthly values of horizontal and vertical force.

Since 1904, mean hourly values of Falmouth declination, inclination, horizontal and vertical force, from the Astronomer Royal's "quiet" days, and diurnal inequalities of these elements for the year, "summer" and "winter." (The 1904 Report also included Falmouth vertical force and inclination hourly means, and inequalities for the year 1903.)

Since 1903, results of absolute observations at Valencia Observatory, and monthly and annual means based thereon.

Meteorological.

Monthly mean values and extremes of air temperature and pressure.

Monthly mean values or totals of vapour pressure, cloud, wind velocity, rainfall, duration of bright sunshine.

Information as to prevalence of wind directions and different kinds of weather.

In 1908 and 1909, earth temperatures at 1 and 4 feet, and measurements of solar radiation with an Ångström pyrheliometer.

Seismological.

Particulars of the principal movements recorded by a Milne seismograph.

The Transmission of Cathode Rays through Matter.

By R. Whiddington, M.A., Fellow of St. John's College, Cambridge.

(Communicated by Sir J. J. Thomson, F.R.S. Received January 26,—Read March 7, 1912.)

Introduction.

The bare fact that cathode rays lose velocity on passing through matter has been known for some time. Leithauser,[*] who discovered that the loss of speed was much greater for slow than for fast rays, made no attempt to discover a law of transmission. It is interesting to notice that the parallel effect in the case of β-rays is so small that for some time it defied detection;[†] its existence, however, has now been definitely proved, and quite recently has been investigated by W. Wilson[‡] in as careful and detailed a way as at present seems possible. Wilson found that owing to the limitations of his apparatus he was unable to take measurements accurate enough to distinguish between relations of the type

$$v_0^4 - v_x^4 = ax \quad (1) \qquad \text{and} \qquad v_0^2 - v_x^2 = ax, \quad (2)$$

where v_0 is the velocity of the rays incident on an absorbent sheet of thickness x, v_x is the greatest velocity possessed by the transmitted rays, and a is some constant depending on the absorbing material.

Since in these experiments with β-rays the initial velocities (v_0) only ranged between 2·85 and $2{\cdot}48 \times 10^{10}$ cm./sec., it is, perhaps, hardly surprising that the results should be difficult of exact interpretation. In the case of cathode rays it is easy to produce rays comprised in a wide range, since the difficulties presenting themselves are mainly ones of manipulation, which can usually be surmounted.

The Apparatus.

The form of the apparatus is indicated in fig. 1.

Heterogeneous cathode rays from the cathode E suffer magnetic dispersion in the solenoid B; a definite velocity corresponding to deflection through a right angle is allowed to enter D and to traverse a thin metal sheet contained therein. The transmitted rays enter the second solenoid C and again suffer magnetic dispersion, and so have their velocity measured. In this way relations can be obtained connecting the velocities of the incident and emergent rays and the thickness of the absorbing material. Some details of manipulation will now be given, but for a fuller account of the construction and use of the solenoids reference must be made to previous papers.*

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[*] Leithauser, 'Ann. d. Phys.,' vol. 15, p. 283.

[†] Schmidt, 'Phys. Zeit.,' 1907, vol. 8, p. 361.

[‡] W. Wilson, 'Roy. Soc. Proc.,' A, vol. 84, p. 150.

A is a spherical discharge tube cemented as shown to the brass, solenoid-wound cylinder B. The cylinders B and C are vacuum-tight and exactly similar, being 35 cm. long, 10 cm. in diameter, and similarly wound on the

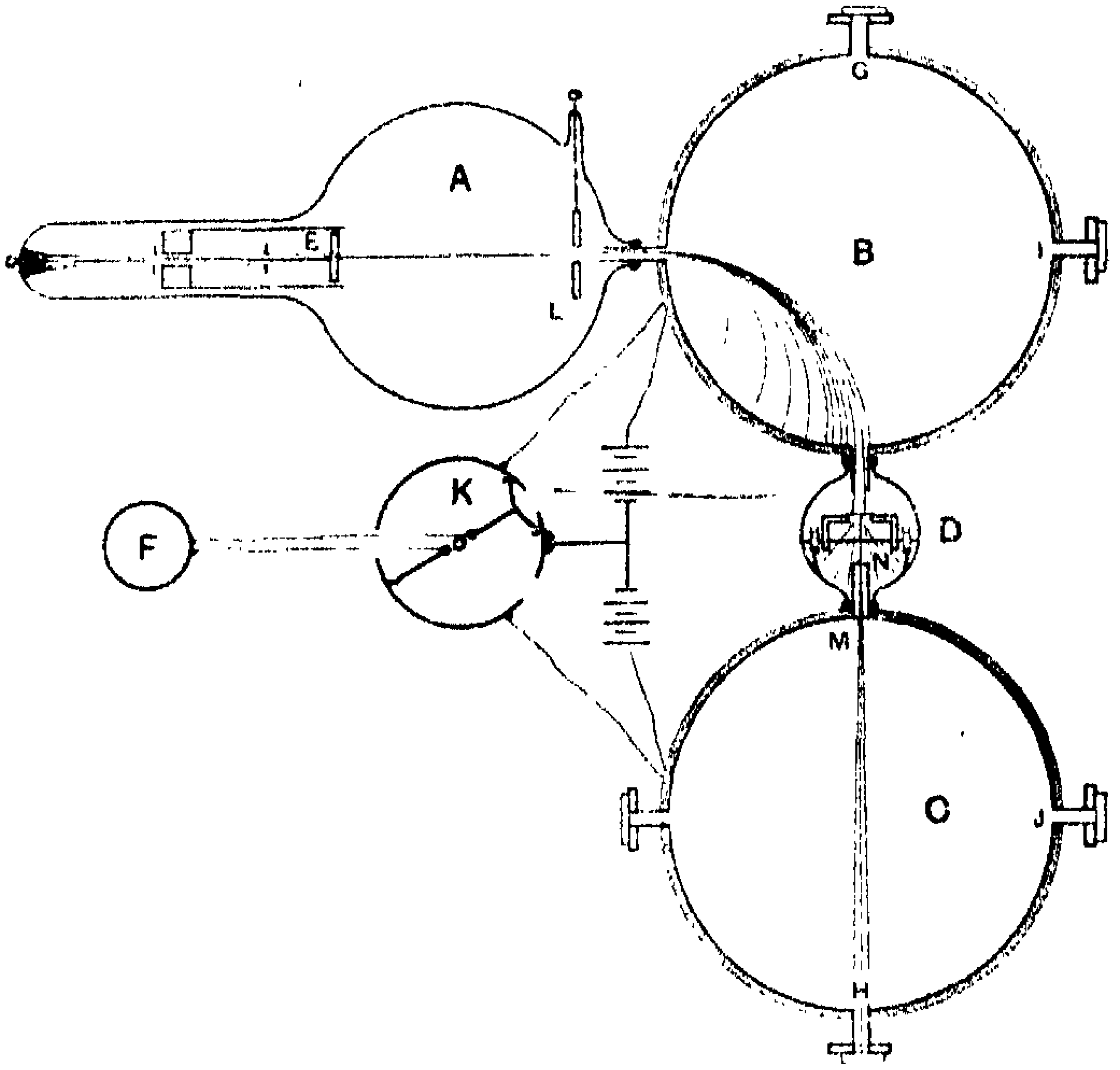

FIG. 1.

outside with insulated copper wire, through which currents up to 10 ampères can be passed. Four narrow brass tubes a few centimetres long pierce each cylinder; neighbouring tubes are at right angles, and the plane in which they lie bisects the axis of the solenoid at right angles. The two solenoids are arranged for convenience with their axes parallel. The glass tube D which connects B and C is about 3 cm. in diameter and 30 cm. long. It is provided with two side tubes fused in as shown, and placed at the centre of the length of the tube. D contains a magnetically controlled trolley of a kind already described,† carrying a number of metal sheets fixed horizontally to a suitable framework. Just below this trolley and fitting closely into the upper tube of the lower solenoid there is a brass tube 5 cm. long, carrying at its ends narrow parallel slits M and N about 0·06 cm. in width. These slits are arranged so as to be parallel to the axes of the solenoids. They are essential because the cathode rays which strike the leaf perpendicularly on its upper surface are completely scattered during transmission so as to move in all directions on emergence from the lower surface, so that it becomes necessary to limit the beam entering C to a very narrow cone.

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* Whiddington, 'Camb. Phil. Soc. Proc.,' 1911, vol. 16, Part II, p. 150; 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 325.

† Whiddington, 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 101.

The interiors of the cylinders are painted with a water emulsion of Willemite, so that the places struck by the rays can be visually observed.

There are two very important adjustments to be made which require some explanation. Firstly, the central axes of the tubes G and H and the centres of the slits M and N must all lie in one straight line, and, secondly, the central normal to the cathode E must pass centrally down the tube I. The second adjustment fulfils the condition for the rays from E (when no current passes round either solenoid) to envelop that diameter of the solenoid B which is at right angles to the diameter HM of the solenoid C. The first adjustment ensures that those rays which have been deflected magnetically through a right angle in B so as to enter and traverse the tube D envelop a diameter of C (this is the state of affairs represented in fig. 1).

Both these adjustments are most easily made by an optical method. A small electric glow lamp is mounted in a brass tube so as to be nearly at the focus of a convex lens, an arrangement giving a sufficiently powerful beam of light for the purpose.*

The first adjustment is made by clamping this collimating system vertically above G so that its axis is parallel to the vertical diameter of B. This will be effected when a uniform circular halo of light surrounds the opening connecting B and D. By gently warming the joints between B, C and D, the cement can be softened enough to allow of slight movements of C and D until the beam of light passes down H. The adjustment is then complete, and the cement is allowed to set in that position. The second adjustment is somewhat easier to make. The collimating system is clamped horizontally opposite I so as to send a beam of light along the horizontal diameter of B, and A is then adjusted until a circular spot of light appears in the centre of the cathode. This means that the centres of E, the aperture in L, and I are in alignment, but it does not mean that the plane of the cathode is perpendicular to this line. This is assured by making the light reflected from the polished surface of E uniformly illuminate the edge of the circular hole in L.

There still remain a few practical details in connection with the measurement of the currents in the solenoids, to which attention must be drawn. The currents required are obtained from two exactly similar sets of "motor cells" connected in opposition as indicated in the figure, the controlling resistance frames not being shown. The specially designed two-way key K makes it possible for the currents in B and in C to be measured by the same ammeter F; in one position of the key the current in B passes through F while that in C passes through a short copper strip, while in the other position the current in C passes through F while that in B passes through the strip. Since the resistances of both ammeter and strip are small in comparison with the resistance of a solenoid, the magnitude of the currents passing is independent of the position of the key—a fact experimentally verified with the help of a second ammeter placed in one or other of the two circuits.

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* It is best to use a slightly diverging beam.

As has been pointed out in a previous paper (*loc. cit.*) a solenoid so short as the ones here used, while largely concentrating the field within itself, sets up a small, but appreciable external field. Such a field can be balanced out at any desired point by means of a suitably placed coil of wire in series with the solenoid. Such a compensating coil does its work whatever the value of the solenoid current, since the external field is always a definite fraction of the internal field, which is itself proportional to the exciting current.

In this particular experiment a rather complicated system of compensating coils is necessary, since there are two solenoids and four places where their external effects have to be eliminated. There are the joint effects of B and C at A and at D, and there are the separate effects of B within C and of C within B. The requisite compensating coils assume rather unwieldy shapes, but prove very satisfactory after having once been set up. They were adjusted with the help of a small compass needle, the compensation being sufficiently complete when, with the greatest current likely to be used passing round the solenoids, the oscillations at the required place were very slow. The effect of the earth's field is in any case very small, and is practically eliminated by arranging for the axes of the solenoids to point east and west.

The apparatus has now been sufficiently described. The current (c_0) in the solenoid B is proportional to the velocity (v_0) of the cathode rays striking an absorbing sheet in D, so that

$$v_0 = \mathrm{G}c_0.$$

Also, if c_x is the current required to deflect the transmitted rays through a right angle in C so as to pass down J, their velocity v_x is given by

$$v_x = \mathrm{G}c_x,$$

the value of the constant G being accurately known.

It is of some interest to compare the dimensions of the apparatus here used with those of the β-ray apparatus employed by Crowther* and by W. Wilson.† It is clear that experiments of far greater accuracy can be performed with cathode rays.

	β-rays.	Cathode rays.
Slit width	1 cm.	0·06 cm.
Radius of path of rays.........	3·5 „	10 „

A really formidable difficulty arises from the fact that cathode rays of the moderate velocity which can be dealt with in this apparatus lose their speed very rapidly in passing through solids. It is necessary on this account to make use of very thin absorbing sheets. The only metals which can be beaten out into leaf appear to be Al, Au, Ag, Cu, Pt, Sn. Of these six metals only Al and Au prove to be suitable for quantitative work, since the others are either too thick or not sufficiently uniform in thickness. It is very necessary to use uniform leaf, because the rays traverse the leaf at one particular point, and the thickness of the material at that point must be taken to be the same as the average thickness of the whole leaf, obtained from a knowledge of its weight and area. The books of leaf as supplied by the beaters contain leaves of extraordinarily equal weights per unit of area, indicating a very good *average* uniformity, yet the individual leaves frequently show considerable local departure from uniformity. It is a *general* uniformity which is so essential and which can only be attained, apparently, in the case of Al and of Au. Unfortunately, both Al and Au are peculiarly liable to rupture under the action of the cathode rays, so that the experiments have to be carried through as quickly as possible. Cu leaf is very much tougher and is accordingly used in any experiments where the actual thickness of the absorbing screen does not require to be known.

Experimental Results.

When there is no absorbing sheet in the path of the rays as they traverse D, magnetic deflection in C produces a sharply defined line of phosphorescence of the same width as the original undeflected one. Moreover, the current in C required to bend round the spot to J has exactly the same value as that in B, showing that the compensating coils are properly adjusted. The interposition of a thin metal sheet in the path of the rays as they pass through D altogether alters the appearance of the deflected beam in C. The single line of phosphorescence is now replaced by a long band or spectrum with a well marked maximum at the extreme high velocity end and gradually tailing off towards the low velocity end. Also the current in C required to cause this maximum to fall on J is perceptibly less than the current passing through B. It is the velocity of the rays comprising this maximum with which the present investigation is concerned.

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* Crowther, 'Proc. Camb. Phil. Soc.,' vol. 15, Part V, found himself able to reduce the slit width to 0·5 cm. with a path radius 4 cm.

† *Loc. cit.*

The following table gives some results obtained by allowing rays of different velocities to fall on a single sheet of Cu. This metal is used for the reason given above, since this particular experiment does not require a knowledge of the thickness of the absorbing material. The first column gives the various values of v_0, the velocity of incident rays, the values of v_x, the velocity of the resulting transmitted beam, appearing in the second column. The third column shows that $(v_0^4 - v_x^4)$ is very nearly constant.

Table I.

$v_0 \times 10^{-9}$.	$v_x \times 10^{-9}$.	$(v_0^4 - v_x^4) \times 10^{-38}$.
5·31	4·59	3·51
6·12	5·72	3·33
6·94	6·66	3·50
7·76	7·53	3·80
8·58	8·45	3·20

The values of v_x given in the above table are each the mean of several observations differing amongst themselves by not more than 1 or 2 per cent.

The next table shows how the velocity diminution depends on the thickness of material traversed. The rays in this experiment were caused to pass through piles of Au leaf of different total thicknesses ranging from one to five leaves, the thickness of each leaf being about 0·00001 cm.

Table II.

Number of leaves traversed (n).	$(c_0^4 - c_x^4)$.	$(c_0^4 - c_x^4)/n$.
1	13·9	13·9
2	30·4	15·2
3	42·2	14·1
5	69·0*	13·8

* This observation can hardly be expected to be of much worth, since 5 gold leaves diminish the *number* of the rays to such an extent as to make it very difficult for the eye even to *see* the transmitted spectrum.

In this table it has not been thought necessary to convert solenoid currents to velocities, so that the second column gives numbers proportional to $(v_0^4 - v_x^4)$; c_0 and c_x are the actual solenoid currents, c_0 being kept constant throughout the experiment. It is clear that the numbers in the second column are proportional to those in the same line of the first column, from which it follows that the relation (1)

$$v_0^4 - v_x^4 = ax$$

is obeyed.*

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* A relation deduced theoretically by Sir J. J. Thomson some years ago. See 'Conduction Through Gases,' 2nd Edition, p. 378.

The law has been tested also for Al and appears to be pretty accurately true; there seems indeed every reason to suppose that the relation is true over quite a wide range of velocities, a point which will be returned to very shortly.

The constant a has been measured as accurately as possible for the metals Al and Au, and comes out to $7{\cdot}32 \times 10^{42}$ and $2{\cdot}54 \times 10^{43}$ respectively.

Thus from (1) it appears that the maximum in the transmitted spectrum of cathode rays of initial velocity v_0, after passing through x cm. of Al, contains rays of velocity

$$v_x = (v_0^4 - 7{\cdot}32 \times 10^{42} \times x)^{\frac{1}{4}}, \tag{3}$$

a formula which will be found later to be of great practical utility.

It is interesting to see whether (1) will bear extension to faster negative particles such as the β-rays used by W. Wilson. In the experiments of this investigator the β-rays from a sample of radium were passed through 0·0245 cm. of Al, their velocity being measured before and after transmission in much the same way as in the present investigation. In Table III some of Wilson's results are compared with the values resulting from an application of (3). The values of the velocities are in every case multiplied by 10^{-10}.

Table III.

v_0.	v_x (observed by Wilson).	v_x (calculated from (3)).
2·565	2·25	2·24
2·735	2·68	2·48
2·818	2·77	2·59

It would appear then that the formula (3) holds so long as the rays move with a speed less than about $2{\cdot}5 \times 10^{10}$ cm./sec.

This is a rather unexpected result, for the velocity loss during transmission must depend in some way on the mass of the transmitted particles, which at a speed of $2{\cdot}5 \times 10^{10}$ cm./sec. has increased by about 50 per cent.

The Transmission of Cathode Rays through Air.

There seems no reason to suppose that the transmission law already proved to be true for metal absorbing sheets should not hold also when the absorbing medium is a gas. It is of particular importance to know the value of the constant a in the case of air, for reasons which will be fully apparent in the next paper, which deals with secondary cathode rays. From the nature of the case it is impossible to use the same method as has been employed in the case of metals, since we cannot compress a given mass of gas into a thin film *in vacuo*. The method which has to be fallen back on is a distinctly inferior one, and cannot give very accurate results; its adoption is the result of necessity.

Broadly speaking, the method consists in causing a stream of cathode rays of known initial velocity to traverse air at a known pressure. The rays gradually lose their speed and eventually become reduced to comparative rest. When this happens, v_x in the formula (1) becomes zero, and we have

$$a = v_0^4/d, \qquad (4)^*$$

in which d is the value of x for which v_x is zero. In the apparatus now to be described d cannot be measured with any great accuracy, so that only an approximate value can be assigned to a.

Cathode rays produced within a discharge tube were first led out into the open air successfully by Lenard, who observed that after escaping through a thin aluminium window, they were able to penetrate several millimetres of air at ordinary pressures. Lenard observed the range of his rays in air by making use of the fact that their track was luminous; in the apparatus indicated in fig. 2, the range of the rays is deduced from the ionisation they produce. It is assumed that a cathode particle may be regarded as having been reduced to rest when it has lost the power of ionising, an assumption perfectly legitimate for the present purpose.

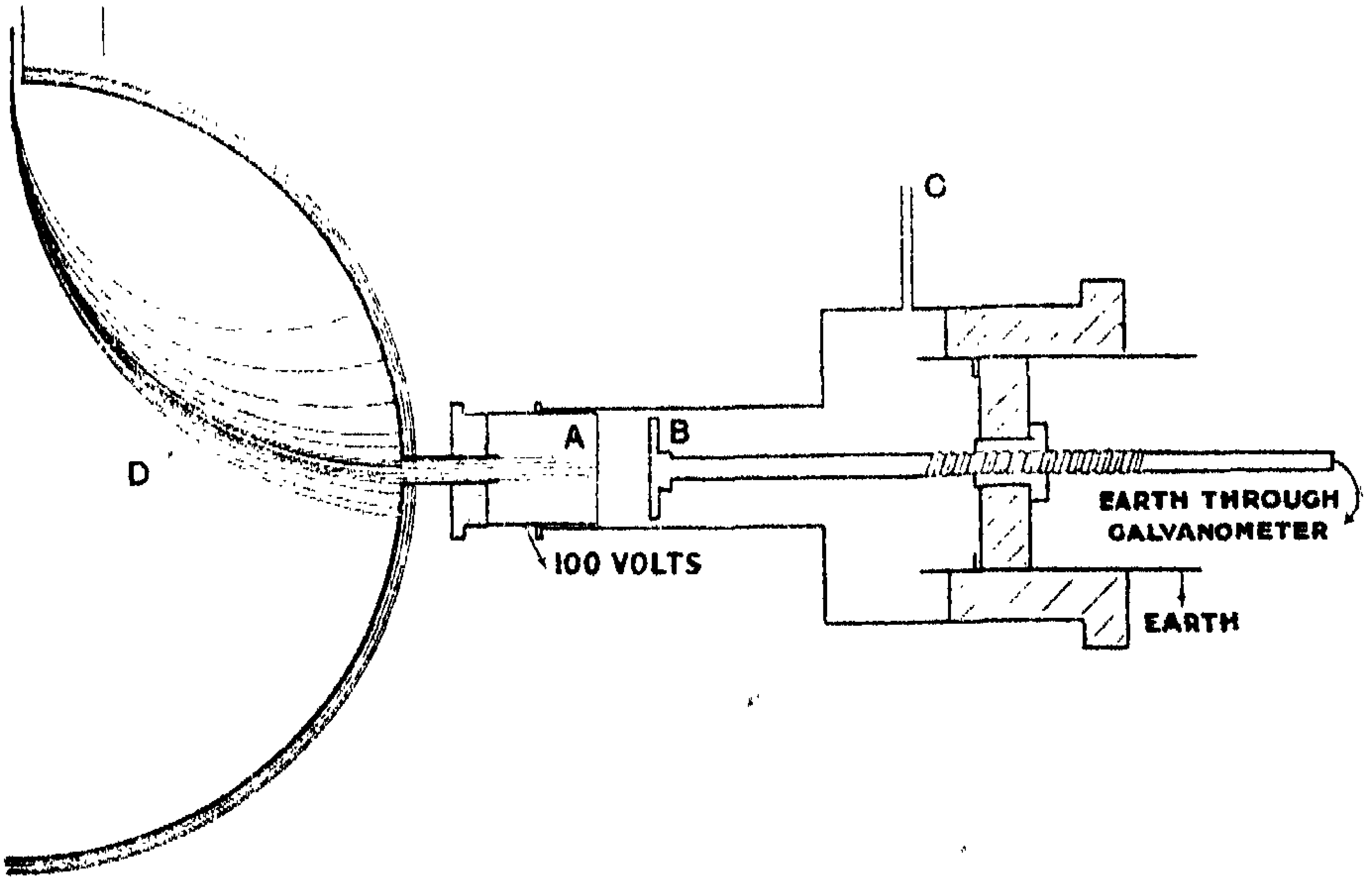

Fig. 2.

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[*] This formula is more fully discussed in the next paper.

The apparatus consists essentially of a small ionisation chamber of brass about 2 cm. in diameter containing a small circular plane electrode B, placed parallel to and at a known distance from a flat plate A pierced with a number of small holes, each about ½ mm. in diameter. A very thin but vacuum-tight Al leaf is cemented over A. The chamber is connected at C to a mercury manometer, drying tubes, and a Fleuss pump, so that the space between A and B can be filled with dry air at known pressures. Homogeneous cathode rays of known velocity are directed on to that side of the window remote from B by means of a discharge tube and solenoid D of the type used in the previous part of this investigation. By suitably adjusting the speed of the rays falling on A, the ionisation produced within the chamber can be made sufficiently intense to measure with a galvanometer. The outside of the chamber and A were charged to a potential of 100 volts, while the collecting electrode B was connected to earth through the galvanometer. From a knowledge of the thickness of the window and the velocity of the incident beam, the velocity of the speediest rays entering the ionisation chamber can be calculated from (3). It is clear that it is this maximum speed which determines d in (4). The apparatus shown in the figure is capable of being used in two distinct ways. We can either alter the distance x between the plates and note when further increase of x at constant pressure produces no increase in ionisation, or we can keep the distance between the plates constant and determine the lowest pressure necessary to yield the greatest possible ionisation. The latter method was adopted on account of its greater simplicity.

If p is this pressure above which the ionisation is independent of the pressure and P is the normal atmospheric pressure, then

$$d = bp/\mathrm{P},$$

where b is the actual distance between the plates.

Unfortunately, it is impossible to construct really satisfactory pressure-ionisation curves (as Beatty has done, using secondary cathode rays) from which to determine p with accuracy, the reason being that it is not possible to keep everything steady long enough to go over the whole curve.

The method finally adopted was to start with the pressure high enough to completely absorb the rays and then to exhaust the chamber very gradually. The galvanometer deflection remains constant until the pressure p is reached, when it commences to diminish. By taking the mean of a number of observations a probable value for p can be arrived at. It is very important to work with the rays as fast as possible, since p is then as large as possible, and consequently errors in observation are of the least possible account.

This method, however, is almost certain to give too low a value for p, and consequently too small a value for d. Thus the value of a deduced from (4) is, from this cause, at any rate, in all probability too large.

There is one rather curious experimental difficulty which deserves particular mention.

When the pressure on the thin Al windows is that due to the atmosphere, the leaf (which, by weighing, is only 0·000432 cm. thick) takes up a permanent concave form. The distance between A and B thereby increases, and not only so, but the thickness of the windows must be diminished, because the material has been permanently stretched to a larger area. The central elements of the windows appear to be depressed about 1/10 mm. below the general level of A, a rough estimate, arrived at by focussing on the window with a high-power travelling microscope. The distance b was therefore taken to be 0·41 cm. instead of 0·40 cm.; there is room here, of course, for some error. Now, it is very important to know the thickness of the windows, because it enters into the expression (3) from which the velocity of the rays entering the ionisation chamber is calculated. We can form an approximate estimate of the diminished thickness of the windows by assuming their sagged form to be spherical and calculating their new areas. If this is done, then it comes out that they are reduced in thickness from 0·000432 to 0·000348 cm.

Now it follows from (3) that unless $v_0^4 > 7{\cdot}34 \times 10^{42} \times x$ no rays can penetrate the window.

This affords an entirely different and, perhaps, more satisfactory method of determining the thickness of these little windows. It is merely necessary to increase the velocity (v_0) of the rays until they are just able to penetrate through to the ionisation chamber. This was found quite easy to do, since, on account of the low speed of rays to be used, the apparatus gave very steady readings. A curve was drawn connecting the ionisation between A and B with the velocity of the incident cathode stream. The curve bent very sharply upwards at a certain velocity, this value is the proper one to substitute in the relation

$$x = v_0^4/7{\cdot}32 \times 10^{42}.$$

Found in this way, x comes out to 0·000340 cm., a value in very close agreement with that found above from geometrical considerations (viz., 0·000348 cm.).

The value 0·000340 cm. for the thickness of the window is used in calculating a, the mean value of which comes out to be

$$2{\cdot}0 \times 10^{40}.$$

Unless there are unsuspected sources of error, this value of a for air should not be more than 15 per cent. from the true value.

Summary.

It has been found experimentally that a cathode ray moving with velocity v_0 can possess, after traversing a thickness x of material, a velocity v_x given by the relation

$$v_0^4 - v_x^4 = ax,$$

where a is a constant depending on the nature of the material.

This constant a has been measured for Al, Au, and air at 760 mm. pressure of mercury and 15° C., with the following results:—

Al	$7{\cdot}32 \times 10^{42}$
Au	$2{\cdot}54 \times 10^{43}$
Air	$2{\cdot}0 \times 10^{40}$

There seems to be no simple law connecting the value of a with the density or atomic weight of the absorbing material.

The Velocity of the Secondary Cathode Particles Ejected by the Characteristic Röntgen Rays.

By R. Whiddington, M.A., Fellow of St. John's College, Cambridge.

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Introduction.

When a metal plate is "illuminated" by Röntgen rays, part of the energy of these incident rays is converted into high-speed secondary cathode particles, which are ejected from the plate in all directions. The mere detection of this emission of negative electricity is an easy matter, since the illuminated plate, if insulated *in vacuo*, charges up positively. By measuring the rate of charging, it would be possible to determine the number of particles ejected per second, while by applying an electric force of such a magnitude and in such a direction as to stop the emission, it might be thought that their speed could be measured. In practice, however, this method of measuring velocities is restricted to slowly moving rays, such as are produced, for example, by ultra-violet light. The particles ejected by

Röntgen rays have in most cases a speed corresponding to a potential fall through many thousands of volts, and at present it is not possible to perform accurate experiments with potentials of this magnitude. Quite the best way of determining high velocities is the magnetic deflection method, in which a magnetic force of known strength is applied to a fine beam of the moving particles in such a way as to act at right angles to their direction of motion; from observations of the curvature of the path described by the particles their speed can be calculated. This method, unfortunately, is at present impossible in the case of secondary cathode particles, since their intensity is never sufficient to allow of their being formed into anything like a narrow beam.

There is, however, a method of attacking the problem which it is the object of this paper to outline. The experimental data available are somewhat incomplete, and the conclusions drawn from them of necessity share this incompleteness.

The method is based on the fact that the secondary cathode particles ionise the gas they happen to be traversing, an effect which may be quite large with a small number of particles, since each particle is capable of producing very many ions before being brought to rest.

Now it is known that the distance d which a cathode particle can travel through a gas depends on its initial velocity v_s, so that if the exact form of the relation

$$d = f(v_s)$$

were known, it would be possible to calculate at once the velocity of a cathode particle whose range was known. I have attempted to work out this idea, using some experiments of Beatty and of Sadler to furnish values for d, and the experiments of the preceding paper to indicate the form of the relation $d = f(v_s)$.

The terminology introduced by Prof. Bragg will be used. For example, the Röntgen radiation characteristic of Sn will be referred to as the Sn X-rays, while the cathode particles ejected by Sn X-rays will be termed Sn cathode rays.

Beatty and Sadler have, independently, and by slightly different methods, investigated the variation of the ionisation produced by a stream of cathode particles as the thickness or effective thickness of the stratum of air they traversed was altered.

Sadler[*] actually altered the depth of his ionisation chamber by using a movable plane collecting electrode. Beatty[†] adopted the superior plan of

[*] Sadler, 'Phil. Mag.,' March, 1910.

[†] Beatty, 'Phil. Mag.,' August, 1910.

altering the *effective depth* by varying the pressure of the gas between two parallel electrodes a fixed distance apart. The effective depth (referred to in future merely as the depth) is proportional to the pressure.

In both methods parallel plate electrodes are supported opposite each other with a saturating electric field set up between them. The high potential plate is "illuminated" with a characteristic Röntgen radiation, and consequently a stream of cathode particles proceeds towards the other insulated electrode, ionising the intervening gas. It is this ionisation which is measured.*

The type of curve which is obtained by plotting I, the ionisation, against x, the depth of the chamber, is shown in fig. 1.

When x is greater than d, none of the particles reach the opposite plate, so that, increasing x above this value d does not increase I, which assumes a steady value, depending on the intensity and type of the exciting rays.

Beatty's results will be referred to most frequently, so it is convenient to point out here that what he actually tabulates is t, the distance between his plates necessary (at 760 mm. pressure of mercury and 15° C.) to give half the greatest possible ionisation, and a quantity λ proportional to $1/t$.

It must be possible to represent the experimental curve of fig. 1 by an expression containing terms which take into account, firstly, the fact that the velocity of the cathode particles is continuously diminishing as the distance traversed increases, and, secondly, the fact that some of the particles may get reduced to rest (by becoming permanently lodged within a molecule or in some such way), thus converting their energy suddenly into heat instead of completing their ionising career.

Such terms would be $$v_s^4 - v_x^4 = ax, \dagger \qquad (1)$$

where v_s is the velocity of a particle at the moment of projection from the plate, v_x is the velocity after traversing distance x, a is some constant depending on the nature of the gas; and

$$N = N_0 e^{-\gamma x}, \qquad (2)$$

where N_0 is the number of particles emitted per second by unit area of the illuminated plate, N is the number crossing unit area a distance x away, γ is some function of x.

It appears that the expression

$$I = k_1 \int_0^x e^{-\gamma x} (v_s^4 - ax)^{\frac{1}{2}} \, dx \qquad (3)$$

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* For the method of allowing for that part of the ionisation due to the Röntgen rays, reference must be made to the original papers.

† See preceding paper on cathode ray transmission.

represents Beatty's curves extremely well. The constant k_1 depends on the initial number of the cathode particles.

Relation (3) may be regarded as empirical, since the hypotheses on which its deduction depends seem unjustifiably simple.

It follows at once if we assume—

(1) That all the rays starting from the illuminated plate have the same velocity v_s, which cannot be the case, since the ejected particles must, some of them, have started from below the surface.

(2) That the ionisation produced in a thin layer of gas is proportional to the energy of the travelling particles, an hypothesis not in accord with some experiments carried out by Glasson,[*] from which it follows that, at any rate, over part of the range here considered, the ionisation is proportional to the *inverse* of the energy.

(3) That γ is a constant, an obviously improbable assumption.[†]

The fact remains, however, that (3) fits the experimental results very well, and it seems an interesting illustration of the possibility of suitably combining erroneous hypotheses so as to arrive finally at a correct formula.

(3) as it stands is not in a form suited to evaluation, but by making the substitution

$$v_s^4 - ax = a/\gamma \, . \, z^2$$

it assumes the form

$$\mathrm{I} = k_1 (a/\gamma^3)^{\frac{1}{4}} e^{-v_s^4\gamma/a} \left\{ \int e^{z^2} dz - z e^{z^2} \right\},$$

which lends itself readily to evaluation, since e^{z^2} can be obtained from mathematical tables, while $\int e^{z^2} . dz$ has been tabulated by Dawson.[‡]

In order to compare the form of the curve represented by (3) with that obtained experimentally, it is necessary to take a special value of v_s. It is convenient to take the case of the Zn cathode rays, the velocity of which will be shown later on to be $6{\cdot}3 \times 10^9$ cm./sec. A suitable value for γ turns out to be 29.

The constants in (3) become therefore

$$v_s = 6{\cdot}3 \times 10^9, \qquad a = 2 \times 10^{40}, \qquad \gamma = 29.$$

Now $e^{-v_s^4\gamma/a}$ is practically constant except very near the origin of the curve, so that to simplify the calculation one can so choose k_1 as to make

$$k_1 (a/\gamma^3)^{\frac{1}{4}} e^{-v_s^4\gamma/a} = 1, \quad \text{in which case} \quad \mathrm{I} = \int e^{z^2} dz - z \, . \, e^{z^2}.$$

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[*] Glasson, 'Phil. Mag.,' November, 1911.

[†] Without making this assumption, (3) would not lend itself to ready transformation and evaluation. It will be seen, however, that γ is absent from the formulæ, (4) and (6), expressing the main results of this paper.

[‡] Dawson, 'Lond. Math. Soc. Proc.,' 1898, vol. 29, p. 519.

The following table shows the dependence of I on x, using only positive values of z. The expression (3) has its greatest (real) value when $z = 0$, *i.e.* when $x = v_s^4/a = 0{\cdot}079$ cm.

The numerical value of the constant of integration C is found by putting $x = 0$ when $\mathrm{I} = 0$.

Table I.

x.	z^2.	z.	$\int e^{z^2}dz$.	ze^{z^2}.	$\mathrm{I} = \int e^{z^2}dz - ze^{z^2} + \mathrm{C}$.
0·079	0·000	0·000	0·000	0·000	10·941
0·05	0·836	0·915	1·250	2·120	10·071
0·03	1·421	1·192	2·108	4·950	8·099
0·02	1·711	1·310	2·675	7·324	6·294
0·0164	**1·815**	**1·348**	**2·977**	**8·390**	**5·580**
0·01	2·001	1·416	3·357	10·600	3·698
0·005	2·146	1·465	3·751	12·620	2·072
0·000	2·291	1·515	4·209	15·150	0·000

The results of this table are shown graphically in fig. 1, the points being marked thus ⊙ ; those indicated by ⊕ are the experimental points of Beatty for the Zn cathode rays.

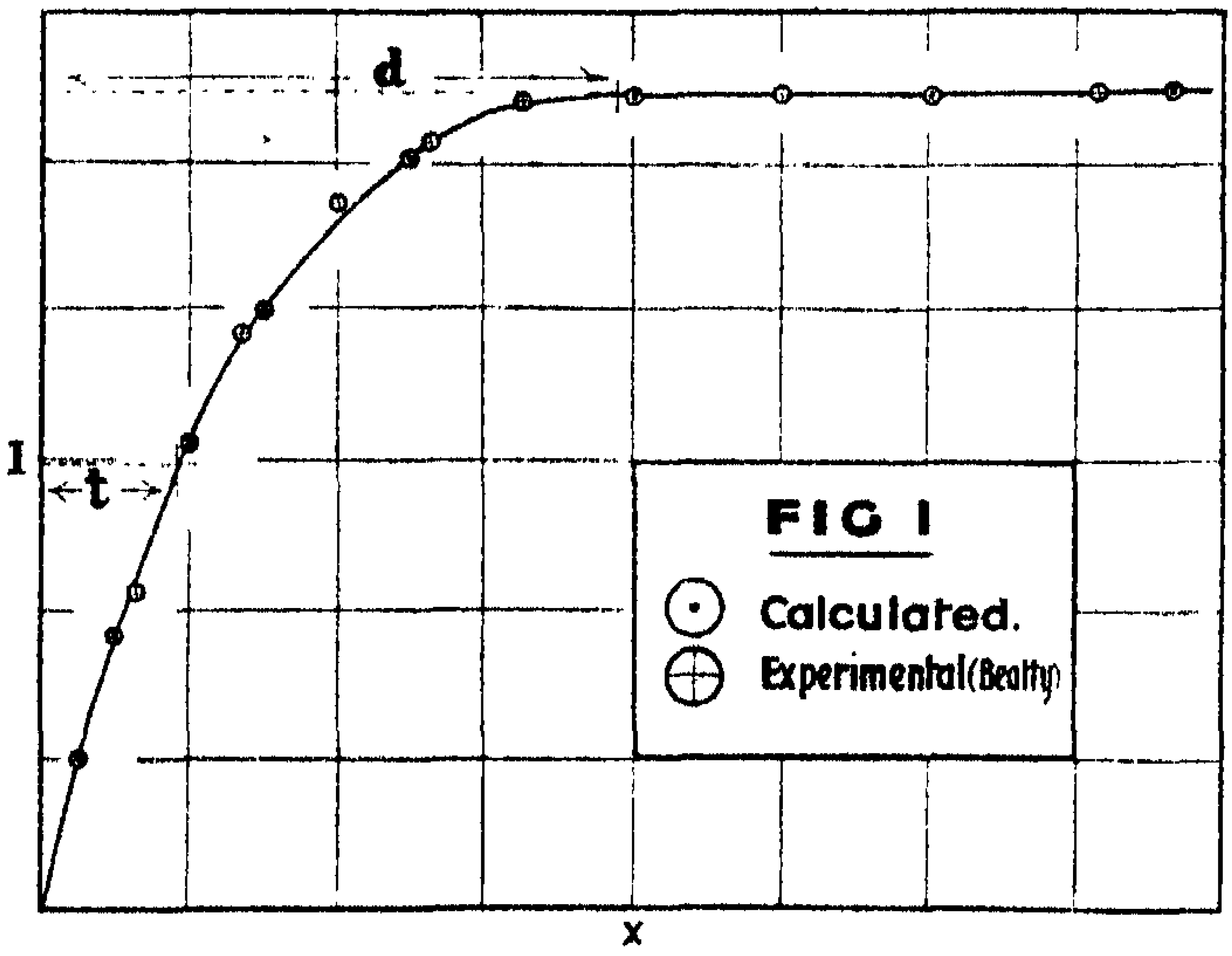


FIG I

As a further test of the accuracy of formula (3) in expressing the experimental results, the value of $x = t = 0{\cdot}0164$ cm. given by Beatty is included in the above table. The ionisation I is seen to be very nearly equal to half the maximum, differing from it by only 1 per cent.

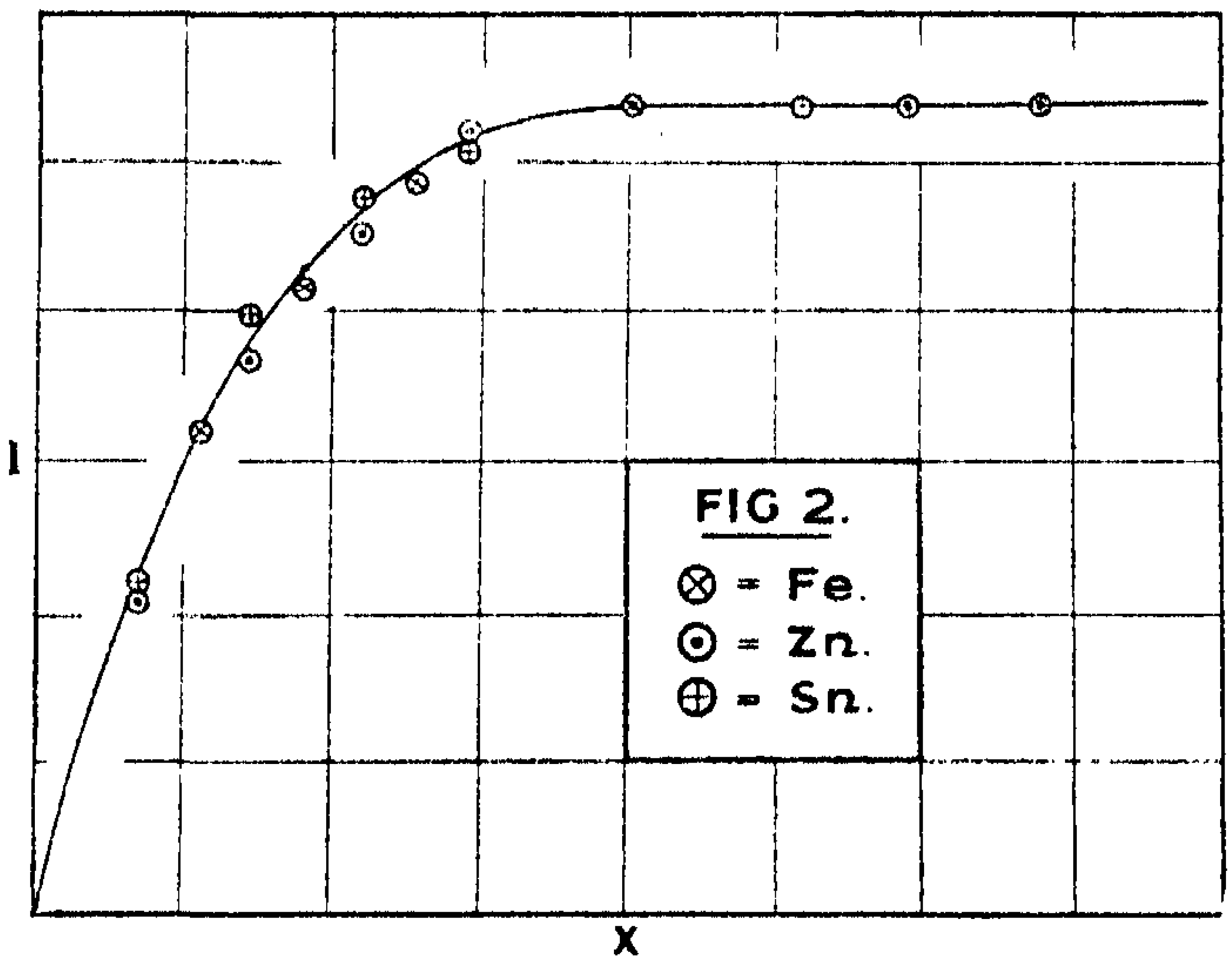
It follows from (3) that the greatest range d of a cathode particle of initial speed v_s is the value of x given by putting

$$v_s^4 - ax = 0, \quad \text{whence} \quad d = v_s^4/a. \qquad (4)$$

So that d is independent of γ.

From this very simple expression it is possible from a knowledge of the range of a cathode ray to calculate the initial velocity.

It has already been pointed out that Beatty and Sadler tabulate a quantity λ which is proportional to $1/t$, t being the thickness of air necessary to reduce the observed ionisation to one-half its maximum value. It is essential, therefore, to get the connection between d and t.



In fig. 2 the experimental curves (Beatty) for the Fe, Zn, and Sn cathode rays are plotted together on the same scale. It is obvious that all the points lie very close to a common curve.

It is, therefore, legitimate to assume that

$$d \propto t \propto 1/\lambda. \tag{5}$$

Combining (4) and (5), we have

$$\lambda v_s^4 = \text{constant}, \tag{6}$$

a relation which affords a ready means of comparing the velocities of the various types of cathode ray.

Application of Relation (6) *to the Experiments of Beatty and Sadler.*

In the following table are collected, for purposes of comparison, the results of Beatty and Sadler. The numbers given are in all cases the values of λ for the various types of cathode ray ranging from the easily absorbed Fe cathode ray to the penetrating Sn cathode ray:—

Table II.

Tertiary radiator.	Secondary radiator.								
	Fe.	Cu.	Zn.	As.	Se.	Sr.	Mo.	Ag.	Sn.
Iron (S.)	—	37·0	35·8	30·2	26·4	21·5	15·8	8·84	6·41
Silver (B.)	87·2	51·9	42·7	27·4	—	—	—	—	3·97
Selenium (B.)	—	—	—	—	—	16·1	14·0	8·8	6·5

This table shows that in only three cases are the two observers in really good agreement, viz., for the Mo, Ag, and Sn cathode rays.

Table III shows that for these three types of ray the relation

$$\lambda w^4 = \text{constant} \tag{7}$$

is true to an accuracy of a few per cent., w being the atomic weight of the radiator supplying the characteristic Röntgen rays :—

Table III.

Secondary radiator.	λ (B.).	λw^4.
Mo	14·0	$1·19 \times 10^9$
Ag	8·8	$1·20 \times 10^9$
Sn	6·5	$1·16 \times 10^9$

It is very unfortunate that the data for the radiators of atomic weight less than that of Mo should be conflicting. It may be noticed, however, that (7) is true for all Beatty's numbers, while it applies to Sadler's only over the limited range Mo—Sn.*

Table IV shows the constancy of λw^4 for the whole of Beatty's range :—

Table IV.

Secondary radiator.	λ (B.).	λw^4.
Fe	87·2	$0·85 \times 10^9$
Cu	51·9	$0·85 \times 10^9$
Zn	42·7	$0·78 \times 10^9$
As	27·4	$0·86 \times 10^9$
Sn	3·97	$0·78 \times 10^9$

Combining (6) and (7), we arrive at the conclusion that

$$v_s = k'w. \tag{8}$$

That is, *the velocity of the cathode rays ejected by a characteristic Röntgen radiation is proportional to the atomic weight of the radiator supplying the Röntgen rays.*

It yet remains to find the value of k'.

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* An examination of Sadler's methods shows that the limitations of his apparatus necessitated the use of a mixture of hydrogen and air for the slower cathode rays, deducing from a density law (assumed) the values of λ for air from those obtained using this mixture. Beatty's results for these slower rays are therefore more trustworthy.

An estimate of its value can be obtained from an examination of Beatty's curves. It is possible to get from them an estimate of d, the range for the Fe, Zn, and Sn cathode rays (the only three for which curves are given), to an accuracy of about 2 per cent. By substituting these values of d in (4) we get the values of v_s given in Table V. From (4) we see that

$$v_s = (ad)^{\frac{1}{2}}.$$

From which it follows that the error in v_s should be not more than about 4 per cent.:—*

Table V.

Characteristic radiator.	d, in cm.	w.	v_s, in cm./sec.
Fe	0·0418	55·9	$5·37 \times 10^9$
Zn	0·0790	65·3	$6·30 \times 10^9$
Sn	0·850	119·0	$1·14 \times 10^{10}$

The constant k' in (8) is thus approximately 10^8.

About a year ago I found an experimental law of the same form as (8), as a result of some work on the production of characteristic Röntgen radiations.† The law referred to can be expressed thus:—

$$v_p = kw. \tag{9}$$

In this formula v_p is the velocity of those primary cathode rays which, striking an anticathode, emit Röntgen rays just sufficiently penetrating to excite the radiation characteristic of the element of atomic weight w. To put it in a slightly different way, the radiation characteristic of the element of atomic weight w is indistinguishable from the hardest constituent of the radiation emitted from a target struck by a stream of cathode rays of velocity equal to kw; k is approximately equal to 10^8. Thus k and k' are very nearly equal, a point of the very greatest interest.

The points brought out in the preceding discussion can be conveniently summarised by following out the various energy transformations taking place between the arrest of the original parent cathode rays within a Röntgen bulb and the subsequent liberation of secondary cathode rays in a distant tertiary radiator by means of characteristic Röntgen rays.

Thus parent (primary) cathode rays of velocity just greater than $v_p = kw$ give rise to primary Röntgen rays, which give rise to secondary Röntgen rays characteristic of element of atomic weight w, which give rise to secondary cathode rays of velocity $v_s = k'w$.

Also, since $k = k'$, we must have, to the same order of accuracy, $v_s = v_p$.

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* Since from the preceding paper a is probably correct to within 15 per cent.

† Whiddington, 'Roy. Soc. Proc.,' A, vol. 85, p. 331.

[*Added February* 20.—Prof. Barkla has recently performed experiments which show that there is more than one characteristic radiation associated with some of the elements. His experiments clearly demonstrate the existence of at least two series of radiations, which he distinguishes by the letters K and L, the latter series being the new one. The present investigation has dealt only with the radiations of series K, but the results can be easily extended to include series L, as will now be shown.

It was pointed out by the writer* that Prof. Barkla's results could be conveniently summarised under one simple empirical formula expressing the fact that so far as Röntgen ray emission is concerned, an element of atomic weight w behaves as though it possessed a variable atomic weight $w' = \mathrm{A}w+\mathrm{B}$, where the values of A and B depend on the series to which the radiation belongs. Now if we define the quality of a Röntgen radiation in terms of the speed of the slowest cathode rays which can excite it, we can state that the radiations characteristic of the element of atomic weight w are indistinguishable from (if not the same as) the hardest constituents of the radiations emitted from a target struck by cathode rays of velocities given by

$$v_p = k(\mathrm{A}w+\mathrm{B}) \tag{10}$$

when A and B are assigned suitable values.†

If we require the radiation of series K

$$\mathrm{A} = 1 \text{ and } \mathrm{B} = 0\text{, so that (10) becomes (9).}$$

If we require the radiation of series L

$$\mathrm{A} = 1/2 \text{ and } \mathrm{B} = -25\text{, so that } v_p = k(w/2-25).$$

In the same way the velocities of the secondary cathode particles ejected by these radiations can be obtained from the formula

$$v_s = k'(\mathrm{A}w-\mathrm{B}). \tag{11}$$

By making the same substitutions for A and B in (11) as in (10), we conclude that if the radiations of both series, K and L, are stimulated in the element of atomic weight w, and the resulting mixture allowed to produce secondary cathode particles, there are two sets of particles produced possessing velocities

$$w\,.\,10^8 \text{ cm./sec.} \quad\text{and}\quad (w/2-25)\,10^8 \text{ cm./sec.}]$$

It gives me very great pleasure to thank Prof. Sir J. J. Thomson for his kind interest in these investigations.

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* 'Nature,' Nov., 1911, p. 143.

† See also 'Camb. Phil. Soc. Proc.,' vol. 16, part 4, p. 329.

The Emission of Electricity from Carbon at High Temperatures.

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(From the National Physical Laboratory.)

Introductory.

This paper is a first communication of the results of some experiments conducted in electric furnaces at atmospheric pressure, and mostly at very high temperatures. The investigation came about originally in an attempt to explain some contamination phenomena which were encountered when short tubes of extremely refractory rare earths were baked in various types of carbon-tube resistance furnaces at temperatures from 1500° C. upwards.

An examination of the refractory tubes after baking showed that, in certain circumstances, the outer surface of each tube, instead of having the white and hard appearance of the rest, was carburised and crumbly. The action was not merely a surface one, but extended to an appreciable depth. On the other hand, the inner surface of the tube was comparatively unaffected, although it was freely open to the furnace gases, nor did the blackening occur if the tube was shielded. An explanation which at once suggests itself is that the blackening was produced by particles—possibly electrified—shot off from the carbon walls of the furnace with sufficient velocity to penetrate the material of the refractory tubes some millimetres (4 to 7) away. The circumstances pointed to the desirability of a general study of the electrical properties of the atmospheres of such furnaces.

Historical.

Negative Electricity.—So far as we know, practically no experiments have been conducted with carbon at pressures approaching atmospheric, but at low pressures the emission of negative electricity from hot carbon has been investigated systematically by O. W. Richardson (1903, *et seq.*),* H. A. Wilson (1904),† Deininger (1907),‡ and very recently by Pring and Parker (1912).§ The ionisation currents have been generally attributed to the liberation of corpuscles from the hot carbon; the magnitude of the effect is largely influenced by the pressure and nature of the residual gas. Richardson obtained from a carbon filament at low pressures currents from 10^{-8} to 2 ampères per square centimetre. He found that the relation between ionisation and temperature for carbon (as well as for some other bodies) could be expressed by the formula*

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* Richardson, 'Phil. Trans.,' 1903, A, vol. 201, p. 497; 1908, vol. 207, p. 1.

† Wilson, 'Phil. Trans.,' 1904, A, vol. 202, p. 243.

‡ Deininger, 'Deutsch. Physik. Gesell.,' 1907, vol. 9, p. 674.

§ Pring and Parker, 'Phil. Mag.,' Jan., 1912.

$$i = a\theta^{\frac{1}{2}}\epsilon^{-b/\theta},$$

where i is the saturated ionisation current, θ is the absolute temperature, and a and b are constants for the substance. (For carbon, $a = 10^{34}$ and $b = 98{,}000$.) Wilson and Deininger each subscribed to Richardson's formula; but Pring and Parker, as the result of experiments on purified carbon at extremely low pressures, impeach the truth of the formula, and affirm that the large ionisation currents obtained by previous observers are due to the emission of corpuscles not from the carbon itself, but rather from some high-temperature reaction between the carbon (or its contained impurities) and the residual gas. Their results show that the negative ionisation from heated carbon falls off continuously both with reduction of pressure and with progressive purification of the carbon.

Positive Electricity.—So far as we know, a similar emission of positive electricity has not been detected with carbon at atmospheric pressure.† But in the case of incandescent metals at atmospheric pressure, Guthrie,‡ as far back as 1873, referred to an experiment which, according to modern views, shows that an iron ball in air at atmospheric pressure emits positive electricity when red hot, and negative electricity when white hot—a result now well known. Elster and Geitel (1883, *et seq.*)‡ got much the same sort of effect with a platinum wire at atmospheric pressure; the ionisation currents were of electrometer magnitude, and their direction and amount were considerably affected by the nature of the surrounding gas.

"*Sputtering.*"—The various phenomena are further complicated by the vaporising or "sputtering" of the hot metal or carbon—an actual transport of material, which is more marked when the substance is negatively charged and the pressure is reduced. The nature of the surrounding gas

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* Richardson's formula, though deduced from theoretical considerations, is of the type which was used by Kirchhoff, Rankine, and Dupré to connect vapour pressure (p) with absolute temperature (θ),

$$\log p = A + B \log \theta + C/\theta.$$

This latter formula, it may be noted, is elastic and allows considerable latitude in the relative values of the constants without impairing its efficiency.

† J. J. Thomson ('Phil. Mag.,' 1899, vol. 48, p. 547) found that a carbon lamp filament gave a positive leak so long as occluded gas was being expelled.

‡ See J. J. Thomson's 'Conduction of Electricity through Gases,' 2nd edit., p. 188, for a complete bibliography.

also affects the disintegration considerably. The carriers appear to consist of small molecular aggregates.* In the case of cathodic sputtering, they are negatively charged.

Thus the electrification produced by an incandescent solid is depends on :—

1. The nature and temperature of the solid.

2. The nature and pressure of the surrounding gas; and it is evident that the phenomena under the conditions of the present experiment will not be of a simple character.

Experimental.

The type of electric furnace employed in nearly all the present experiments consisted of a straight carbon tube heated by alternating current. Some of the details of a small furnace of this type are shown in fig. 1. A

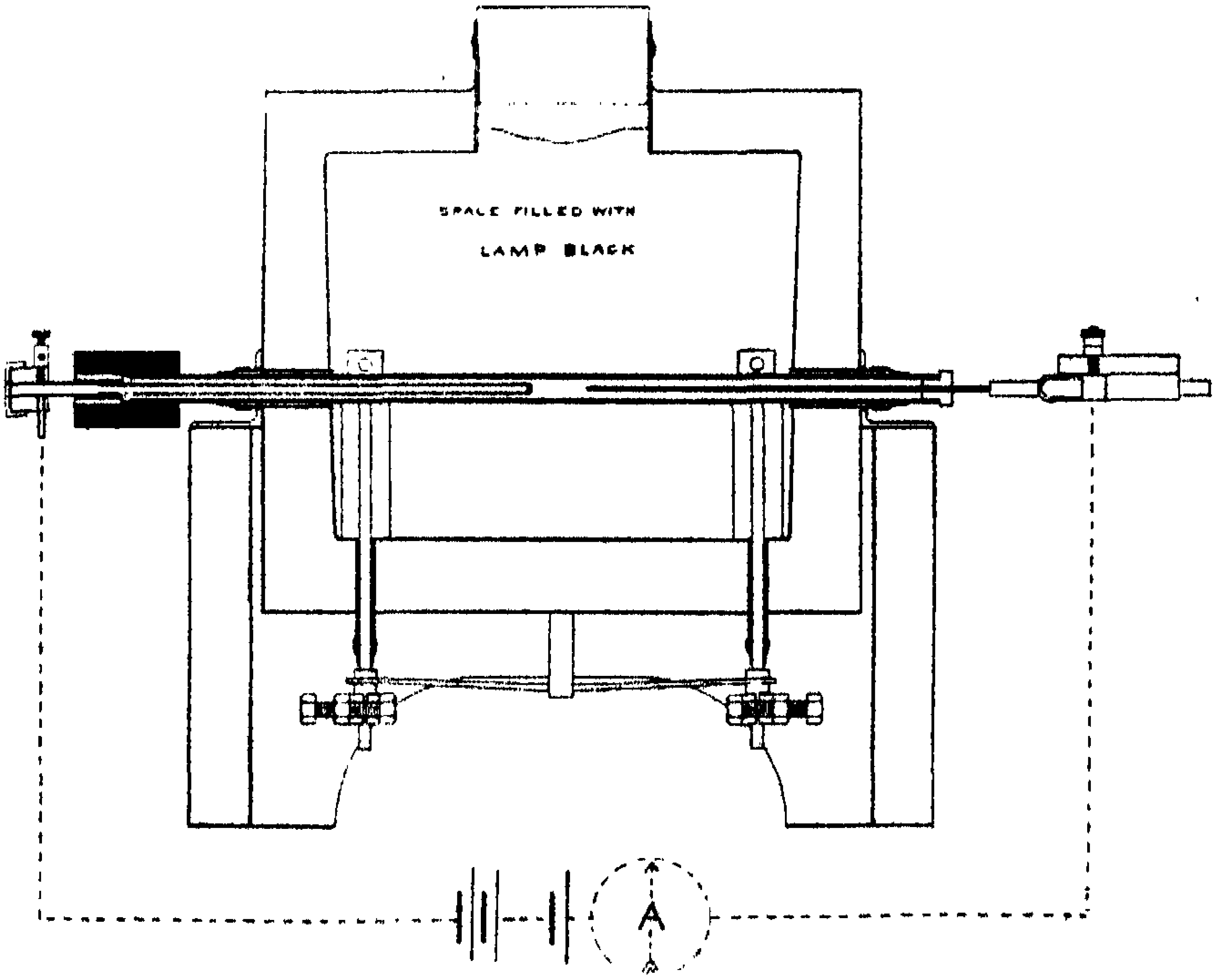

FIG. 1.—Small model Straight Carbon-tube Furnace, with Pyrometer Sighting Tube and movable Electrode in position for Determination of Potential-current Curves.

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* The sputtering of iridium at temperatures from 1400° upwards is notorious, and Reboul and de Bollemont ('Compt. Rend.,' Mar. 20 and Oct. 2, 1911) have recently shown that both copper and silver, when heated in a furnace at temperatures from 500 to 1000° C., give a sputtered image having the outline of the emitting metal on screens up to 2 mm. away in air at atmospheric pressure. No potential was applied. The amount of the deposit increases with the temperature and varies with the surrounding gas. They put forward the view that the sputtering is associated with the known emission of positive electricity when these metals are heated.

second form was made up of a graphite spiral heater having an insulated liner-tube of carbon similar to the conductor used in the first type of furnace. This is illustrated in fig. 2. In both furnaces the heater was surrounded by very pure lamp black, with an outer lagging of magnesia brick.

The *graphite* used in the experiments was the usual grade of Acheson graphite made at Niagara. In one instance, analysis showed it to be of a purity of about 99·8 per cent. carbon. The graphite tubes were drilled from solid rods and after a little experience the heating spirals of the second type of furnace were easily cut from the solid to any dimensions by the use of an appropriate lathe; graphite, unlike amorphous carbon, is an extremely tractable material to machine.

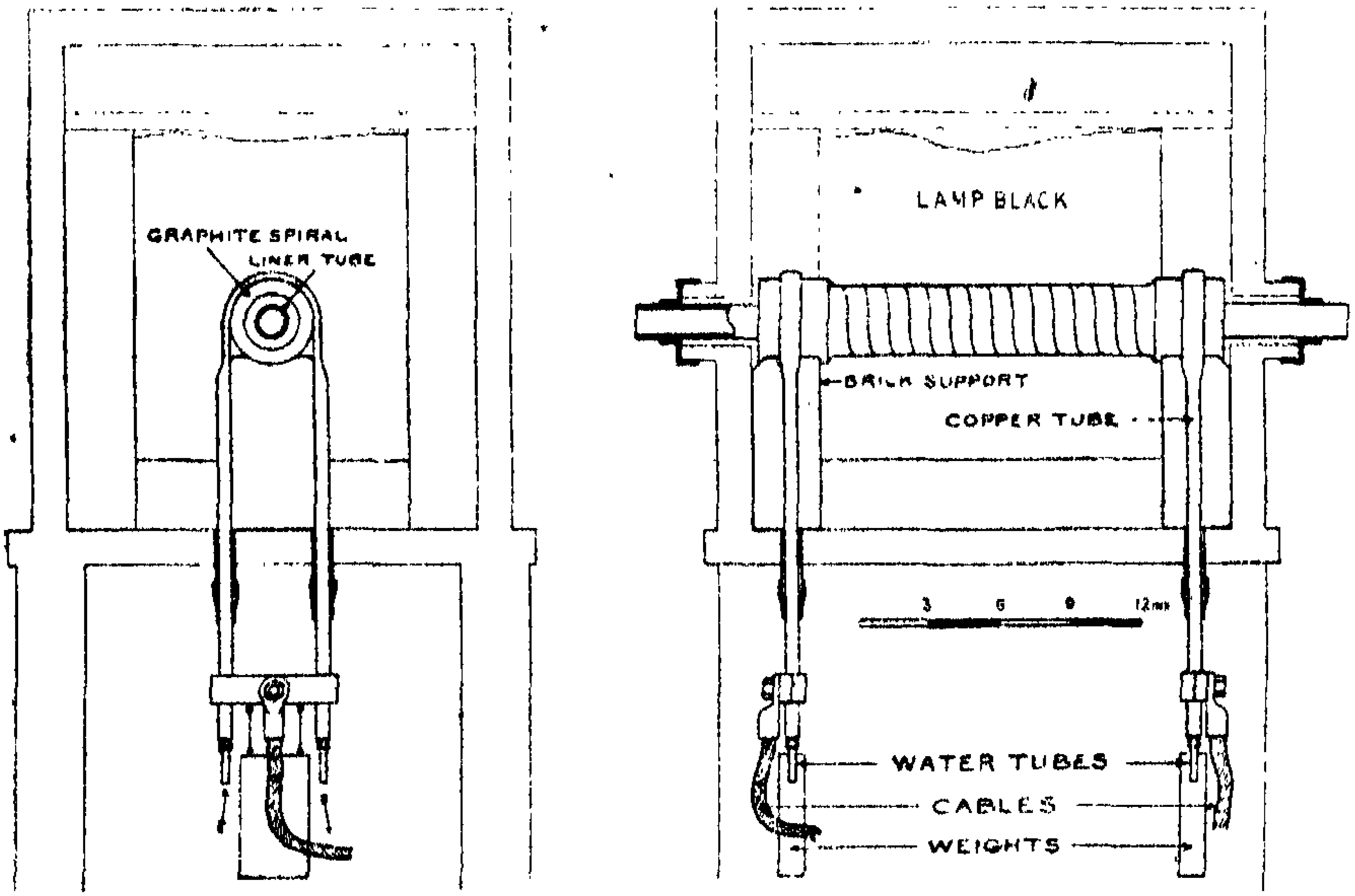

Fig. 2.—Carbon Spiral Furnace, for temperatures up to 2500° C.

The *carbon* tubes were supplied by the General Electric Company's Witton Works, Birmingham, and were of a purity higher than the average, but usually contained a little under 1 per cent. of foreign matter (iron, silica, and alumina). A good deal of this, however, was usually removed previous to use in the experiments by heating for some time to a very high temperature in a current of nitrogen.

The experiments were carried out in the Thermometry Department of the National Physical Laboratory, where a newly installed plant, specially designed for electric furnace work, was to hand. The power supplies available are a 100 volt D.C. circuit, giving currents up to 600 ampères, and a motor alternator of 15 kilowatts capacity with extra large range of regulation and capable of giving voltages up to 500 and frequencies from 80 to 200. Low-frequency alternating current up to 250 ampères at 30 to 60 cycles at a fixed voltage of about 70 can be got from slip-rings on the motor.

By means of a transformer having a number of variable ratios, alternating current can be obtained up to 250 ampères at 20 volts or 2000 ampères at 2 volts. The regulating devices are such that any temperature attainable in a furnace can be kept constant as long as desired.*

Many of the details of this unusually complete equipment are due to Mr. C. G. Eden, now of the Aeronautics Division of the National Physical Laboratory. We wish to acknowledge our great indebtedness to him, not only for his work in this connection, but also for his active co-operation in the earlier experiments.

Potential-current Curves.

The initial experiments were directed to a determination of the current-voltage curves for two insulated carbon rod electrodes projecting within the furnace one from each end, and in alignment, as shown in fig. 1. The distance between them could be varied as desired. By means of copper clips and low resistance leads they were connected at their outer ends† with a battery of variable E.M.F. and a current-measuring device of many overlapping ranges capable of reading from a micro-ampère to 50 ampères. One electrode was hollow and through it was sighted a Siemens optical pyrometer, suitable for the measurement of temperatures up to 3000° C.

Access of air to the interior of the furnace was prevented by thin mica windows, and a current of any required gas, in most cases nitrogen, could be passed through when desired.‡ In all the experiments dealt with in this paper, the pressure remained atmospheric.

With small potentials (up to 6 or 8 volts) applied to the electrodes, no appreciable current could be detected at temperatures below about 1400° C., but as the temperature rose the current became measurable and rapidly increased until at about 2000° it reached a value of several ampères. The highest current recorded was 10 ampères. Fig. 3 will give a notion of some of the curves obtained at different temperatures for electrodes 1 cm. apart. At the lower temperatures the ionisation currents attain—curiously enough for such a high pressure and currents of this magnitude—what appear to be saturation values with quite small applied voltages. As far as the experiments go, the curves at the higher temperatures show the same character with higher potentials; with small voltages, there is a linear relation between potential and current, as will be seen.*

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* A detailed description of the furnaces and other electro-technical equipment used in this research is being prepared for publication elsewhere, and to this source reference must be made for further details.

† The outer ends of the electrodes remained perfectly cool and there was no question of any thermo-electric disturbances between the carbons and the copper leads.

‡ The passage of a current of gas was absolutely necessary while temperature measurements above 1800° were being made, in order to remove the slight fog which always accumulates in the sighting tube if any impurities are present in the carbon.

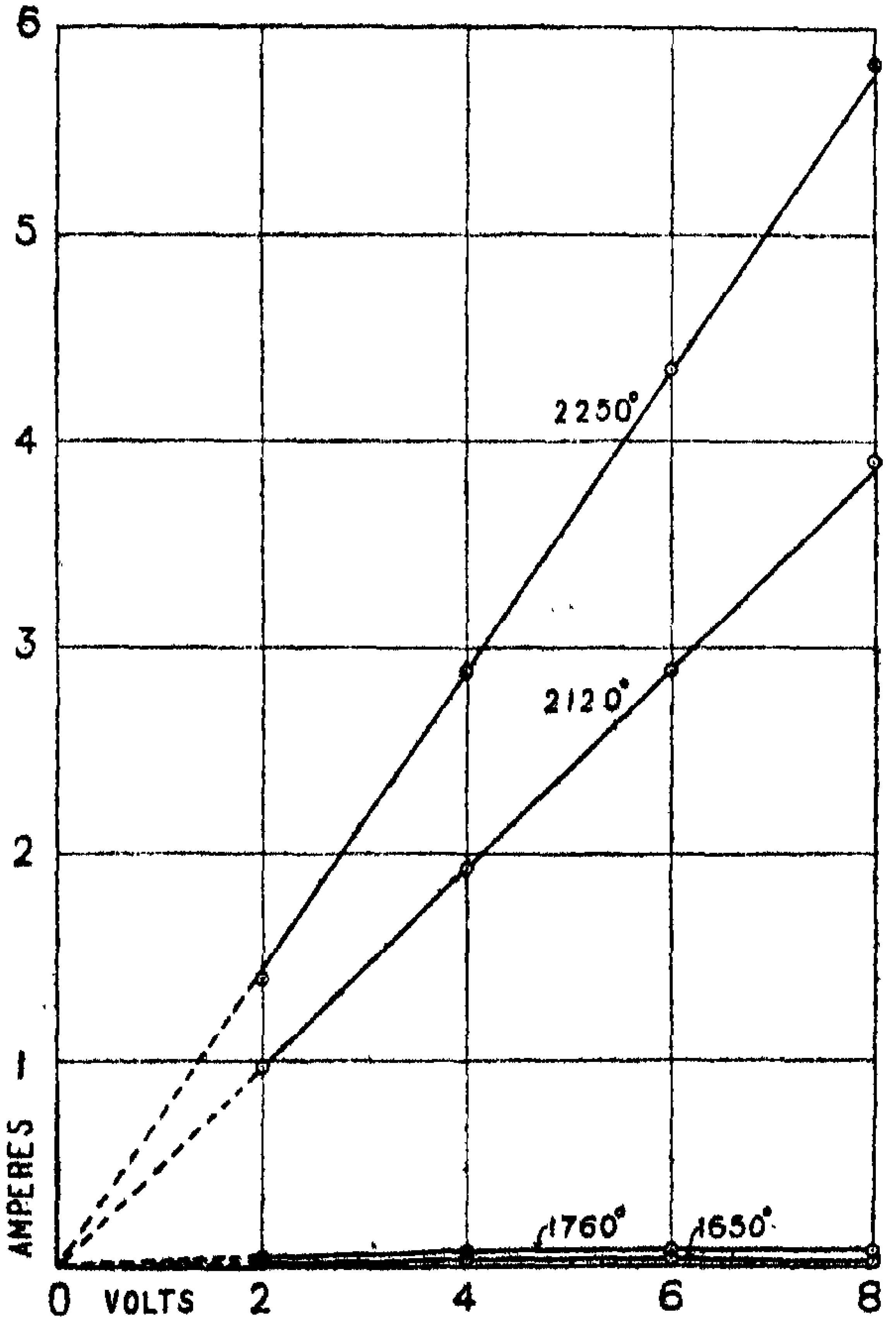

Fig. 3.—Relation between Ionisation-current and applied Potential for a 1-cm. gap between the electrodes.

Ionisation and Temperature.

The continuous curve of fig. 4 shows a relation between ionisation-current and temperature for an applied potential of 2 volts on a 1-cm. gap between the electrodes. As will be seen, the curve is exponential in character,* but as the currents make no pretence of being saturated, the actual numbers have no great quantitative interest. The points indicated (by small circles) were not all obtained in the one experiment but on different days with the same apparatus. The dotted straight line was obtained by plotting the logarithm of the current against temperature.

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* This experiment was shown by Mr. Eden and one of us at the Royal Society Conversazione of May, 1911.

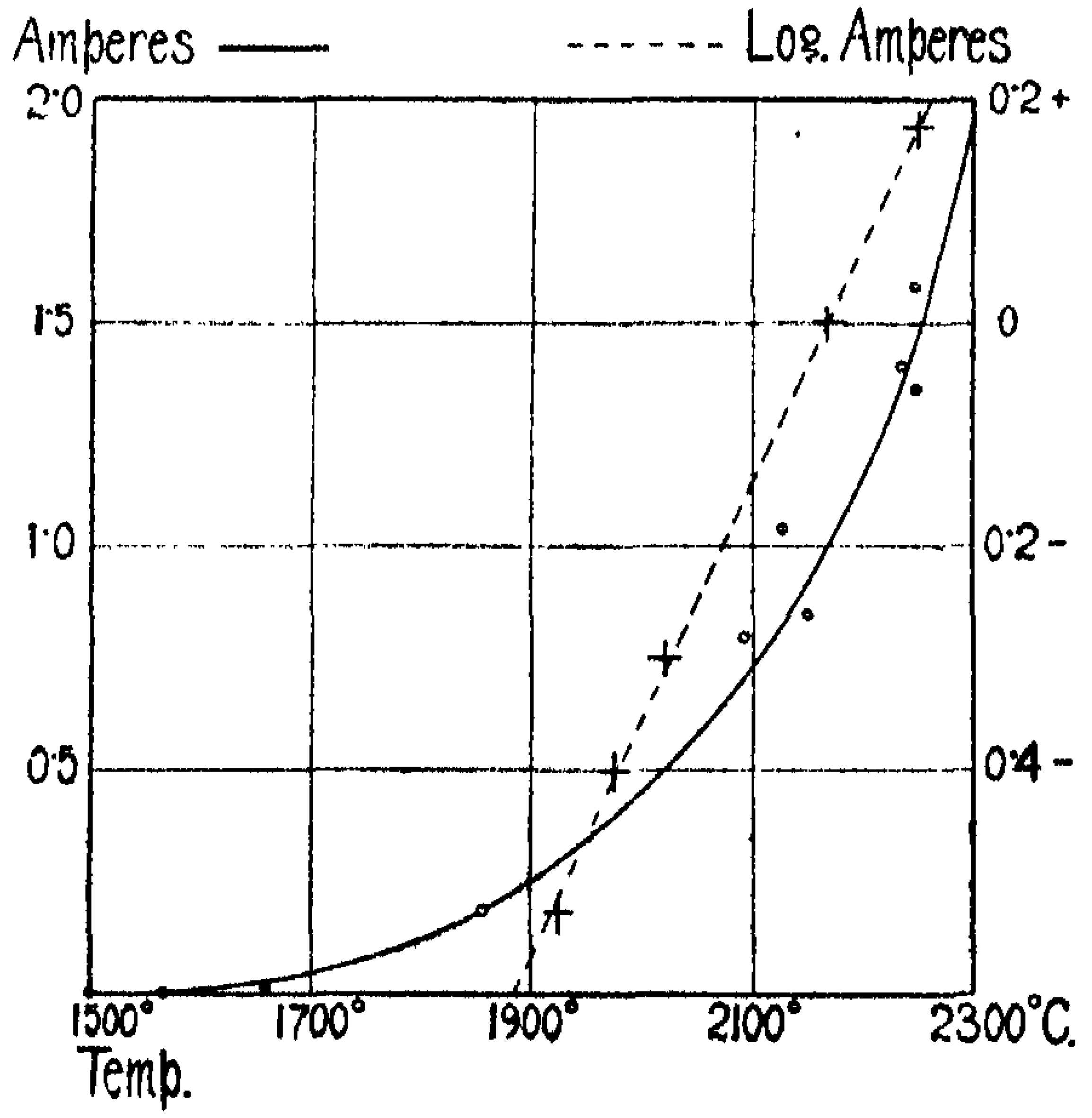

FIG. 4.—The full-line curve shows a relation between ionisation-current and temperature for an applied potential of 2 volts on a 1-cm. gap between the electrodes. The dotted straight line is plotted from log. of the current and temperature.

Ionisation Current and Length of Gap.

The table adjoining indicates how the current varies with the distance between the electrodes for an applied potential of 2 volts. The results are set out in fig. 5. The full-line curves are plotted to the left-hand scale of current; the dotted lines to the right-hand scale. It will be noticed that the effective resistance of the gap increases, but not very much, with the distance between the electrodes. The explanation of this is given later, on p. 388.

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* The curve is very fairly represented by $i = 1{\cdot}55 \times 10^{-4}e^{0{\cdot}00412\theta}$, where i is the current in ampères and θ the temperature on the centigrade scale.

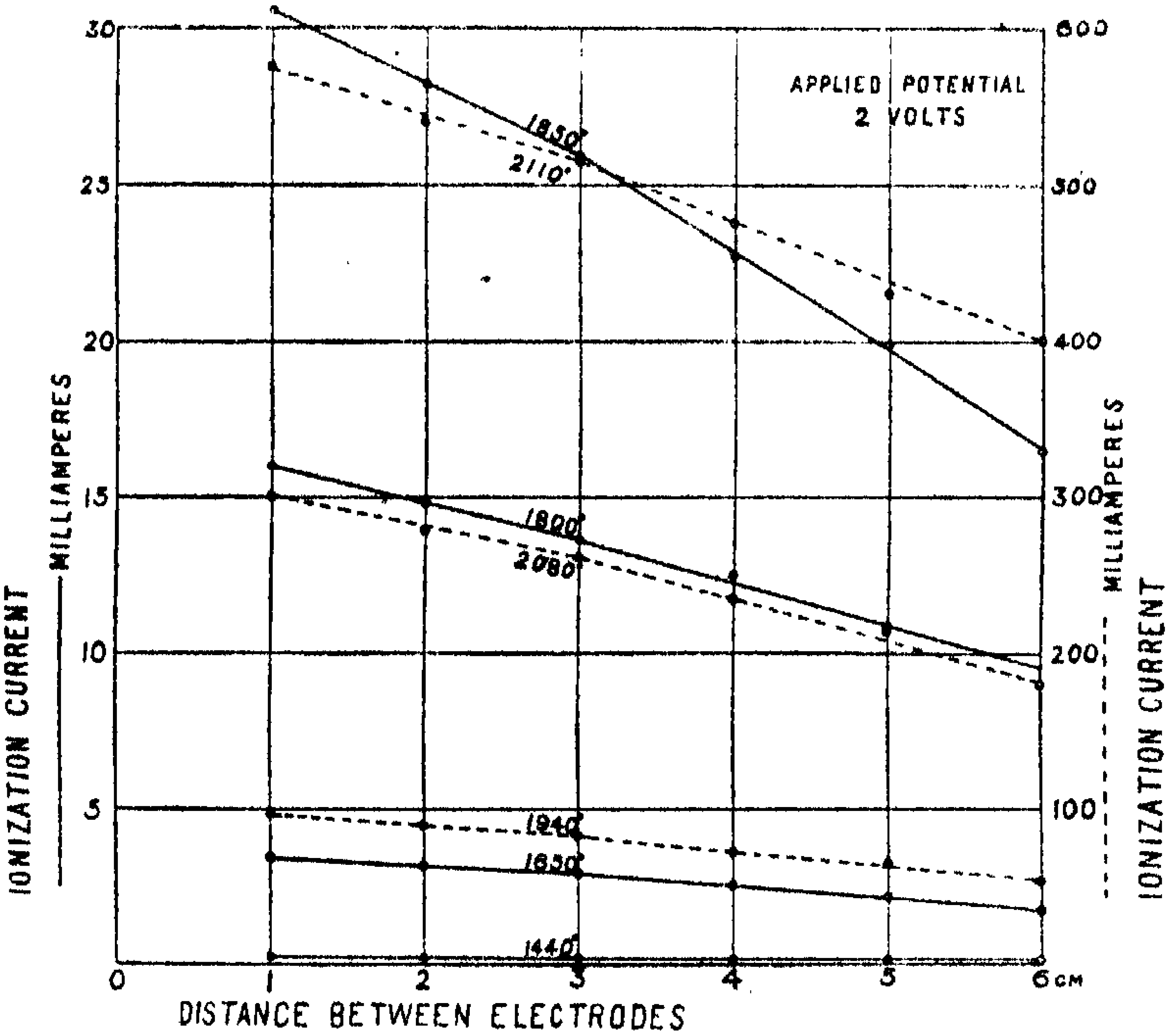

Fig. 5.—Relation between Ionisation-current and Distance between Electrodes for an applied Potential of 2 volts. The full-line curves are plotted to the left-hand scale of current; the dotted lines to the right-hand scale.

Table I.—Applied Potential, 2 volts.

Distance between electrodes.	1440° C.	1650°.	1800°.	1850°.	1940°.	2080°.	2110°.
cm.	milli-ampère.	milli-ampères.	milli-ampères.	milli-ampères.	milli-ampères.	milli-ampères.	milli-ampères.
1	0·22	3·40	16·0	30·6	96·2	301	575
2	0·21	3·18	14·8	28·2	89·5	278	540
3	0·19	2·92	13·6	25·9	82·5	261	515
4	0·18	2·59	12·5	22·7	72·5	234	475
5	0·16	2·20	10·9	19·9	65·2	214	430
6	0·13	1·75	9·0	16·5	54·0	180	400

The Magnitude of the Ionisation.

The magnitude of the ionisation currents indicated that, although the pressure was atmospheric, the atmosphere of the furnace was ionised to an unusual degree at high temperatures. The possibility of some sort of leakage and rectification-effect from the alternating heating current was tested and dismissed, as it was found that the ionisation currents persisted when the furnace current was temporarily shut off. Before testing the effect of temperature in the absence of an external source of potential, we were led to try an experiment in which the furnace tube was heated by direct instead of alternating current. In these circumstances, we found a decided asymmetry in the amount of the ionisation current, depending on the direction of the external potential (which amounted to 2 volts). When the potential was such as to tend to send the current between the electrodes in the same direction as the heating current in the furnace tube, the resulting ionisation current was some four or five times bigger than when the external E.M.F. was reversed; in some cases the inequality was even more marked. Not only that, but the reading of the current-measurer was always in the same direction, no matter which way the outside battery was connected, *i.e.* the potential collected by the electrodes from the furnace was greater than the applied voltage. The outside battery was accordingly cut out, and the galvanometer now revealed currents of from 8 milliampères with a furnace temperature of 1660° to 34 milliampères at 1770°. The explanation is, doubtless, the greater electrical emissivity of the negative end of the furnace tube as compared with the positive end. The electrode within the negative end of the furnace becomes negatively charged with respect to the other electrode, and the resulting potential difference assists or retards the applied E.M.F. in a way which agrees with that actually found.

Hot and Cold Electrodes.

The next step was to try the effect of temperature alone in the absence of any directive influence of the heating current. Accordingly, one of the two insulated carbon electrodes was mounted as before within the central hot region of the alternating current furnace, while the other was arranged on a sliding carriage, so that (with a travel of about 6 inches) it could, at will, be placed either near the fixed electrode or some distance away, in the cooler part of the furnace tube. Thus, each time the movable electrode was shifted a large difference of temperature existed temporarily between the electrodes, and this manifested itself in the ammeter in the circuit as a transient current, which at 1400° amounted to 2 milliampères, and increased to nearly 2 ampères at 2500° C. When the movable electrode was pushed in, the current attained its maximum value pretty rapidly and died away as the two electrodes assumed the same temperature. The direction of the current was such that the cooler inserted electrode was positive with respect to the hotter fixed electrode. When the movable electrode was withdrawn into a cooler part of the furnace a current was again generated, but in the reverse direction. Such a reversal would naturally not follow if the electrodes alone were concerned, but is easily explained if the furnace tube is taken into account. For the radial distance between the electrodes and the furnace tube was only some 8 mm.; so that, when the electrodes were separated, the easier path for the ionisation current was to bridge the two gaps between the electrodes and the furnace tube rather than cross the gas separating the electrodes. The hot fixed electrode remained at the same temperature (and potential) as the surrounding furnace tube and played no direct part in generating the current, but the hot movable electrode after being moved outward would emit negative electricity to the colder furnace tube, resulting in a reverse ionisation current as found.*

Similar results were obtained when the movable electrode was made the fixed, and *vice versâ*, and there was little difference in behaviour if graphite electrodes were substituted for carbon.

In view of the above explanation we carried out a pair of experiments, in one of which the inner ends of the carbon electrodes were inserted into carbon blocks of larger diameter, so that the distance between the electrodes and the furnace walls was reduced from about 8 mm. to 3 mm. In the other experiment the blocks were removed. Keeping the same distance between the electrodes, we found, as we expected, a larger ionisation current when the blocks were present than when they were absent. The currents were also of much longer duration owing to the extra time the blocks took to heat up and cool down. The part the furnace tube plays in these experiments explains the comparatively small variation of the resistance of the gap between the electrodes with its length (see p. 385).

The foregoing experiments were simplified by making a "poker" of a closed hollow carbon (or graphite) tube with an insulated co-axial rod of the same material inside it. When this was inserted into the furnace the outer sheath became hot first and a current passed across the intervening gas in the usual direction, from the cold rod to the hotter tube.

In several of these poker experiments we noticed a small initial "reverse" current, which soon died away and changed into a large current in the usual direction. This reverse current is doubtless due to positive ions which were emitted at the lower stages of the heating. The effect was not always obtained, and our experience up to now in these and further experiments has been that it is most marked with new carbon and diminishes with repeated heating. This is also the experience of workers with other substances than carbon; many experimenters, indeed, maintain an intimate connection between the emission of positive electricity and the evolution of absorbed gases, such as CO. In the case of carbon it may be related to the expulsion of some of the gaseous or more volatile impurities.

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* By means of a device giving a suitable periodic movement to one electrode, a current generator constructed on this principle was shown at the reading of the paper.

Non-electric Heating.

We felt that it would be of distinct interest to try to get some of the results put out above by methods of heating other than electric. The poker experiment last referred to was accordingly repeated, using a Méker gas furnace giving a temperature of about 1600° C. The largest negative* current obtained was 10 milliampères. Positive currents as large as 20 milliampères were also recorded, but owing to the oxidising nature of the atmosphere some combustion of the outer carbon tube occurred, and the results were at times a little obscure.

A second arrangement was tried in which the outside of a small poker (constructed essentially as before) was subjected to the flame of an oxy-acetylene burner. This has a temperature of some 2400° C. at the tip of the inner cone and is the hottest of all known flames. The heating was uneven and the currents obtained were unsteady; the highest value was about 1 milliampère in the usual direction, with occasional small "positive" currents.†

Water-cooled Electrodes.

We were now naturally desirous of converting the transient currents of the above experiments into steady currents, and to this end the following new arrangement was employed. An insulated brass tube, through which was sent a rapid current of water, was arranged along the axis of the furnace, and formed a cold electrode. The hot electrode was a surrounding co-axial insulated carbon tube, which received its heat from the furnace. The radial distance between the electrodes, both of which were stationary, was about 5 mm. and into this space hydrogen was continually passed, as it is known that this gas facilitates the passage of ions. As before, the electrodes were connected externally through a current-measurer and no potential was applied. The observations for a steadily rising temperature are shown in fig. 6. The carbon electrode was new and the first current recorded by the galvanometer was one which would be produced by positive ions crossing from the hot to the cold electrode (see p. 388). Afterwards the current reversed, attained a maximum in 17 minutes, and then dropped considerably. From 22 minutes onwards the current progressively increased with temperature and was in the neighbourhood of 0·4 milliampère for the last five minutes of the run, which had to be terminated owing to overheating of the furnace transformer, which at this stage was being greatly overloaded. On taking down the apparatus, the brass tube was found to be coated over most of its length with a deposit of carbon thick and coherent enough to be slid off in short lengths. Towards one end of the tube the deposit was rarer and whitish—presumably silica. This evidence of the distillation of both silica and carbon at atmospheric pressure is important. We associate the maximum negative current shown in fig. 7 with the passage of silicon and other impurities which are volatilised at about 2000° C. out of the carbon electrode. On a second heating, the maximum does not occur, and the ionisation current increases steadily with temperature. The transference of carbon from the hot electrode to the cold may prove to be a complete explanation not only of the contamination phenomena mentioned on p. 379, but also of the comparatively large accompanying currents. The point is being worked at and, should it appear that the ionisation currents

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* *I.e.*, in the usual direction, from the cold electrode to the hot across the gap.

† We have since found that Dubs tried a similar experiment as long ago as 1888 ('Centralblatt. f. Elektrotechnik,' vol. 10, p. 749). He played a blowpipe flame on the lower of two carbon plates, one above the other and 1 mm. apart, and found (by the use of a "galvanoscope") that a weak current flowed from the cold to the hot plate across the gap. The effect was less with copper plates and was not detectable with iron.

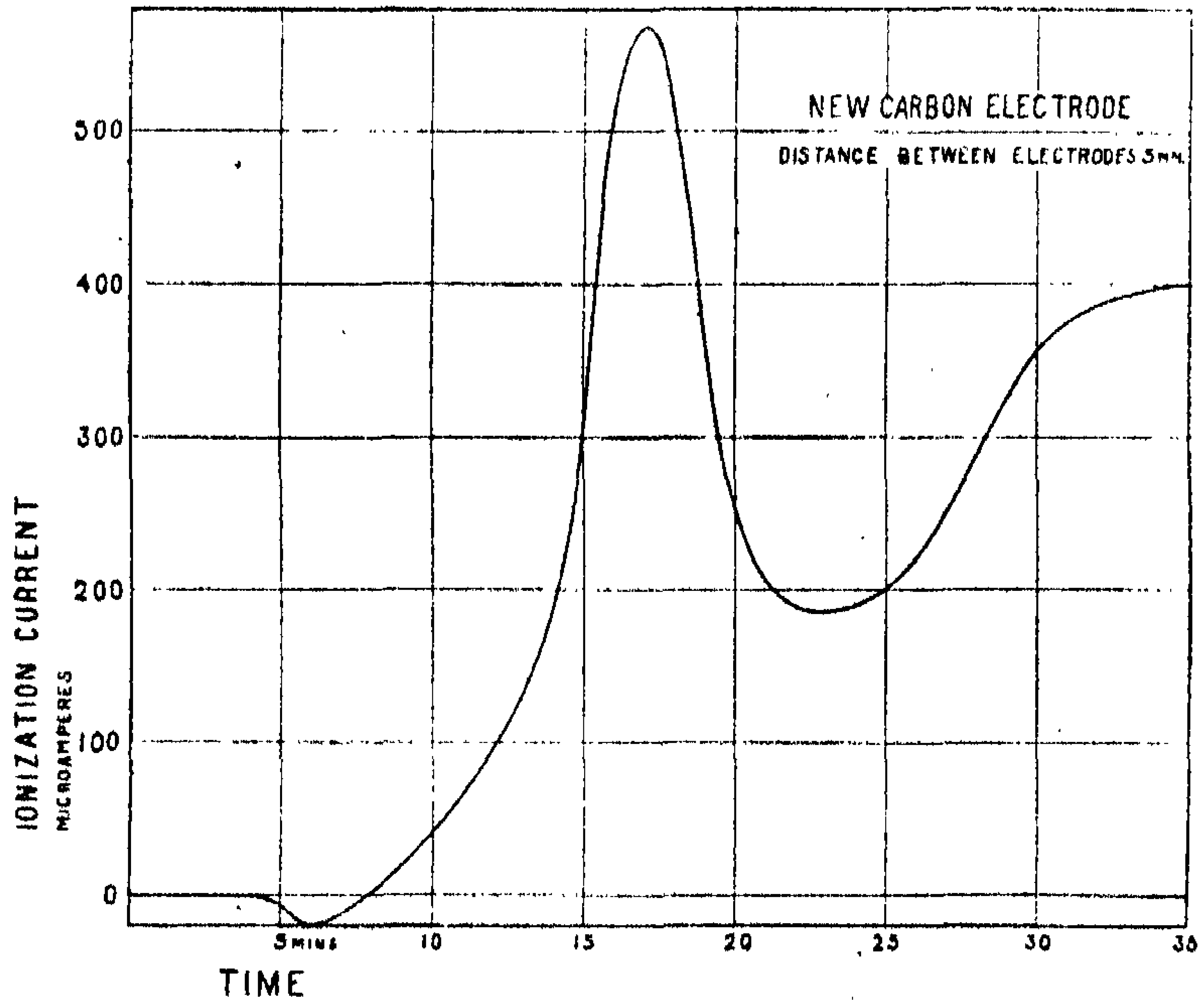

FIG. 6.—Relation between Ionisation current and Time with a steadily rising Temperature. The "cold" electrode was water-cooled; the "hot" electrode was of new carbon. No potential was applied.

are due almost wholly to carbon vaporised or sputtered in this way, the experiment could probably be modified so as to yield an average value of the ratio of the charge to the mass for the carriers concerned.

It was apparent that the comparative smallness of the ionisation currents in the last experiment was due to insufficient temperature-difference between the electrodes, and steps were taken to remedy this. The furnace tube was taken out, and thinned over a short central region so as to render the heat, with the power available, more local and intense. The transformer was fitted with an air blast arrangement to keep it cool. The walls of the outer carbon electrode (which were rather thick) were also thinned considerably over the central region.

In the new run, neither positive rays nor a "negative" maximum was detected, but there was a general increase in the negative ionisation, the highest steady value being about 20 milliampères with the furnace near its upper limiting temperature of about 3000° C. A copious supply of hydrogen was found to be beneficial; the flow required nice adjustment, as too much gas cooled the furnace and was as bad as too little.

The Gas between the Electrodes.—Some interesting results came to light when the gas between the electrodes was varied. The following figures are abstracted from the note book :—

Rough value of temperature of hot electrode.*	Atmosphere.		
	Hydrogen.	Nitrogen.	Residual† furnace gas.
° C.	milliampères.	milliampères.	milliampères.
2000 ?	10	9	6
2300 ?	17	12	10
2400 ?	19	14	12
2500 ?	20	13	15

* In this particular arrangement, temperature measurements of any sort were very uncertain, and the figures given above must be considered only as the roughest estimates.

† Neither H_2 nor N_2 was supplied.

So far as these experiments go, there is not much difference between nitrogen and hydrogen at the lower temperatures; there is more at higher temperatures. But perhaps the most interesting feature of the observations is the large momentary increase in the ionisation that was obtained when a new gas was admitted into the space between the electrodes, *e.g.*, when hydrogen was admitted the current would leap up momentarily to half as much again as its ultimate steady value. The same thing occurred when nitrogen was the new gas. Now it is well known that acetylene, cyanogen, methane, etc., can be synthesised at such temperatures, and it seems probable that on the entry of a new gas into the furnace momentary synthesis occurs when the proportions of the components are favourable, and that this production of C_2H_2, CH_4, C_2N_2, NH_3, or the like, is evidenced by an increase in the ionisation of the atmosphere. We hope to investigate this point further.

This particular experiment terminated eventfully in the fusion of the brass tube electrode. It was interesting to note that most of the water which streamed into the furnace (which was then at about 3000° C.) was immediately dissociated into hydrogen and oxygen, which burnt at one end of the furnace in a large blue flame, 2 feet long, coloured green at times with the vapour of brass.

Later Experiments.

In order to enhance the effect still further we have tried various modifications of the apparatus. To augment the electrode difference of temperature the hot electrode was removed, as we found that with alternating heating current the furnace tube could without prejudice be used as the hot electrode, provided, of course, that the "ionisation circuit" was carefully insulated. The brass water-cooled tube was sheathed with a larger carbon tube which served as the cold electrode, the whole being mounted as before along the axis of the furnace. The general cooling of the furnace was reduced in consequence, and with this arrangement we have obtained in different experiments steady currents of as much as 0·8 ampère for a few minutes, 0·2 ampère for half an hour, and 0·1 ampère for over an hour.

Fig. 7 illustrates one run obtained in a nitrogen atmosphere with new carbon electrodes. As the temperature rose, an initial small positive current of a few micro-ampères was succeeded by a large negative maximum amounting to 0·8 ampère. This diminished afterwards to about 0·1 ampère, and at this stage the furnace temperature was steadied, and a constant ionisation current was obtained for over an hour, in fact, until the experiment was arrested. The potential difference which developed between the electrodes during this time amounted to 1·8 volts.

While the large negative maximum was being recorded we noted that the blue flame of the escaping gases from the furnace tube was tinged yellowish—an effect attributed to silica vapour which was carried along with the stream of gas. The yellow colour disappeared when the current dropped to its steady value.

On a second run with the same apparatus neither positive rays nor a negative maximum was observed.

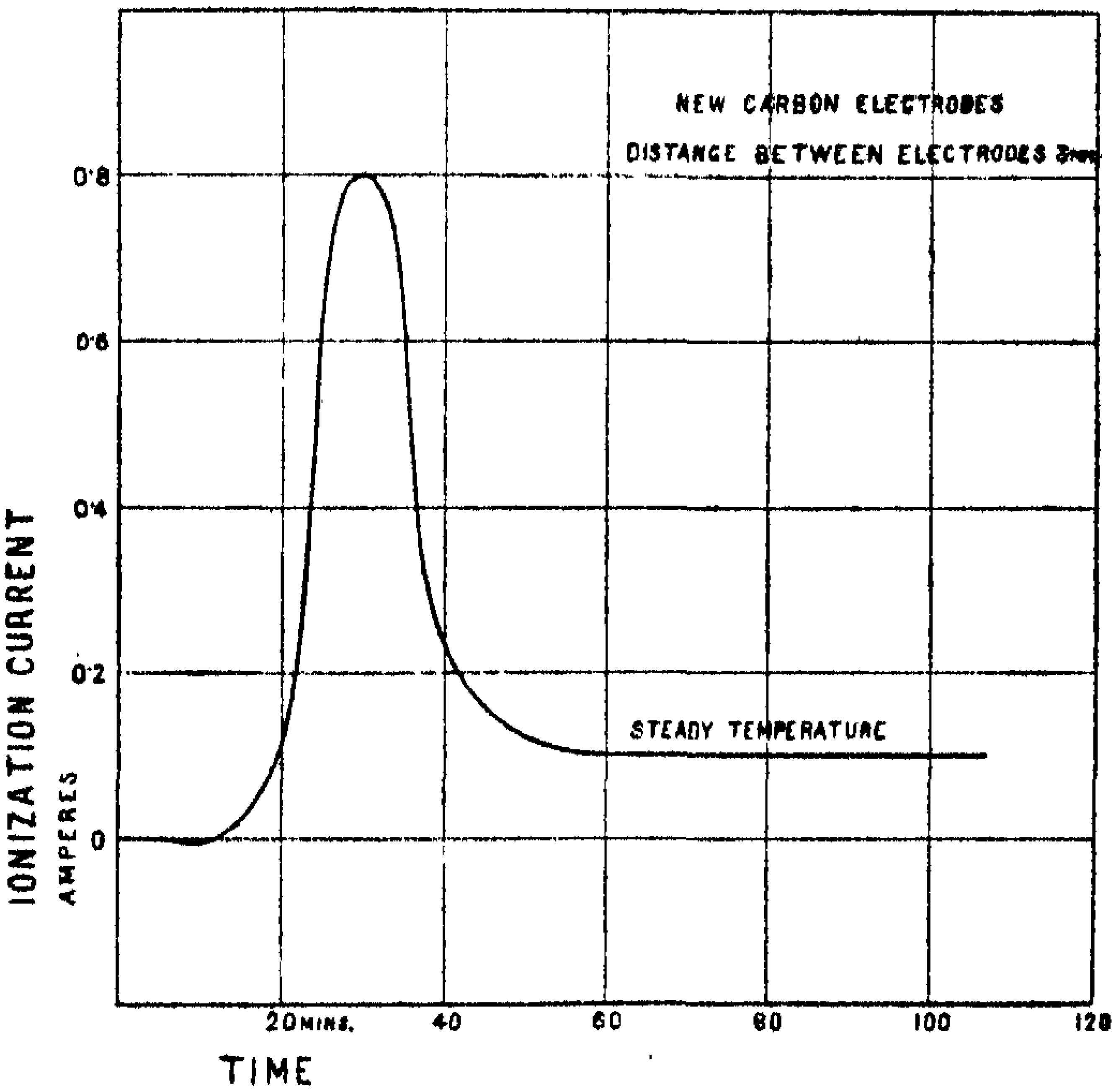

FIG. 7.—Relation between Ionisation current and Time for two new Carbon Electrodes, one hot, the other water-cooled. No potential was applied. The temperature was rising for the first 50 minutes and was afterwards steady.

Discussion.

Although we have not as yet any definite knowledge of the nature of the carriers of electricity concerned in the foregoing experiments, we should like to offer a few comments on the results. It may be that these carriers are almost wholly sputtered solid matter and that corpuscles do not play a great part in the phenomena as they do at low pressures. According to Richardson, the ionisation currents obtained with carbon in high vacua are due solely to the emission of corpuscles; the only part the surrounding gas plays is to become ionised by collision and so augment the current. In some of the present experiments no potential was applied to the electrodes, and if the corpuscles owe their velocity of emission only to the temperature, such velocity at 3000° C., for example, is about 3×10^7 cm. per second* (assuming with J. J. Thomson the applicability of the gas laws and the kinetic theory to the unattached electrons which are disseminated through solids). This speed is a very slow one: corpuscles liberated by ultra-violet light are more than 10 times, cathode rays over 100 times and some β-rays nearly 1000 times as fast. In gases at atmospheric pressure the free path of such unencumbered electrons would be very small indeed, and their ability to ionise by collision would be negligible according to present theory. We have, of course, to remember that a rise of temperature produces a fall of density, with a corresponding increase in the free path, *e.g.*, at 2000° C. the "effective" pressure is reduced to about 1/8th; at 3000° C. to 1/11th. Experiments with a vacuum furnace would probably throw much light on the matter, and such experiments are now in progress in a furnace in which the prevailing pressure can be adjusted to any desired value.

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* Equivalent to a potential fall of about $\frac{1}{4}$ volt.

As we have remarked elsewhere, our largest ionisation currents appear to be associated with the expulsion of impurities in the carbon, and probably the magnitude of the effects would be modified if impurities were wholly absent.

Carbon has the faculty of holding tenaciously enormous amounts of foreign matter, particularly occluded gases, and if the evolution of these impurities* goes hand in hand with the emission of negative electricity some ultimate steady fatiguing of the carbon should be found. Our experience does not enable us to say whether this is so; up to now we have noticed nothing of the kind. Much the same ideas have been expressed by Messrs. Pring and Parker in their paper already referred to. In this connection reference should be made to an important paper by W. C. Arsem in vol. 20 of the 'Transactions of the American Electrochemical Society,' in which the relation between the rate of graphitisation of carbon and its contained impurities is thoroughly studied. The view hitherto held that graphitisation of carbon is generally accelerated by the presence of impurities such as iron oxide derives no support from his experiments.

Apropos of the effect of impurities, the large currents obtained by Richardson with an over-run carbon glow-lamp may be largely due to the ejection at such a high temperature of the various impurities contained in the carbon and binding material of the filament. It is well known that, in lamp practice, it is only of recent years that it has become customary to heat carbon filaments either before or after mounting (except during the flashing process) to much more than about 1700° C., at which temperature some of the possible contained impurities are only slightly volatile. We hope to repeat all the present experiments with spectroscopically pure carbon and graphite.

In considering the chemical side of the phenomena described in this paper, it should be remembered that the relative activity of various gases changes rapidly with temperature. For example, CO_2 at 2500° behaves as an energetic supporter of combustion, and acts on carbon not very differently from oxygen at low temperatures. Nitrogen, which at ordinary temperatures is regarded as inactive, becomes, at high temperature, an agent of attack for many metals and other substances. Many compounds, such as steam, cannot exist at really high temperatures, and are probably completely dissociated.

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* Cunningham ('Phil. Mag.,' 1905, vol. 9, p. 193) found that an electric discharge at low pressures was transmitted more easily by nitrogen freshly expelled from carbon than by ordinary nitrogen.

It may be noticed, in passing, that the experiments set out above, in which no potential was applied, afford an interesting example of the Thomson effect for a vapour. The currents brought about by the potential gradient flow in the direction opposite to the heat flow. In the case of carbon "vapour" this agrees with what is known for the solid. It is worth recording that the atmosphere of the furnace appeared, as far as could be seen, to be perfectly clear when the carbon "vapour" was crossing the space between the electrodes.

It would at once occur to anyone who had been occupied with considerations such as have been detailed in this paper that it might be possible to construct on some such lines a generator of electricity which would depend directly upon combustion at high temperatures; and, naturally, this is an aspect of the question of which we have not lost sight.

Summary.

An investigation into the electrical properties of the atmospheres of carbon-tube resistance furnaces has been undertaken at temperatures from 1500° to 3000° C., and at atmospheric pressure.

(1) Potential-current curves have been derived by the use of two exploring electrodes of carbon or graphite. At high temperatures, currents up to 10 ampères were obtained with the application of quite small potential differences (up to 8 volts) between the electrodes. The ionisation increases exponentially with the temperature.

(2) In the absence of any applied potential a reversible transient electric current was obtained by keeping one of the electrodes fixed in the furnace and heating or cooling the other electrode by moving it in or out of the hot region of the furnace. The highest current thus obtained was nearly 2 ampères. The production of an alternating current was thus rendered possible by the use of a suitable periodic device.

(3) If both electrodes are stationary in the furnace and one is kept permanently hot and the other (by water-cooling) permanently cold, a continuous current can be maintained without applying potential, *e.g.*, a steady current of 0·8 ampère has been obtained for a few minutes, and 0·1 ampère for over an

hour. These are "negative" currents, *i.e.* they flow from the cold to the hot electrode across the gap. Their magnitude is somewhat greater in hydrogen than in nitrogen.

(4) These large negative currents appear to be intimately associated with the transit across the electrode gap, first of the impurities in the carbon, and afterwards of the carbon itself.

(5) Small "positive" currents of a few micro-ampères have been detected with new (but not with old) carbon electrodes at the lower stages of the heating.

(6) Some of these effects have also been obtained from non-electric sources of heat.

The Wave-Problem of Cauchy and Poisson for Finite Depth and slightly Compressible Fluid.

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(Communicated by Prof. A. E. H. Love, F.R.S. Received February 1,—Read February 22, 1912.)

1. *Introduction.*

The present paper is in some respects a completion of a former paper* on water waves resulting from a given disturbance. The following article is devoted to a numerical discussion of a solution, previously given, of the normal Cauchy-Poisson problem for finite constant depth of fluid. The last part of the paper contains a detailed treatment of compressible fluids, with a view to elucidating the initial stages of the spreading out of a disturbance initially confined to a limited region of the fluid. It is found that a very general case of propagation is capable of formal solution.

2. *Numerical Discussion of the Cauchy-Poisson Problem for Finite Depth.*

The serial solution given in the previous paper lends itself to a certain extent to numerical treatment, though not so well as for the case of infinite depth, which has been so completely discussed by Lamb.† In the general case there does not seem to be any general transformation to facilitate the calculation, so that we have to rely on the direct use of the series. The solution referred to may be briefly recapitulated as follows:—

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* 'Roy. Soc. Proc.,' A, 1910, vol. 83, p. 347.

† H. Lamb, 'Proc. Lond. Math. Soc.,' Series 2, 1904, vol. 2, p. 371.

Let the motion be in two dimensions x, y, and let h be the constant depth of the fluid. It is required to find the elevation η at time t at a point distant x from the origin on the free surface $y = 0$, when the motion is caused by the release from rest at time $t = 0$ of a mass of fluid of cross-section Q heaped up on a very small base near the origin. Writing ϕ_λ for $\cot^{-1}(2\lambda h/x)$, and $\{n, \lambda\}$ for the coefficient of x^λ in the expansion of $(1+x)^n(1-x)^{-n}$, we have

$$\frac{\pi x\eta}{Q} = -\Omega_1\left(\frac{gt^2}{2x}\right)+\frac{\Omega_2}{1.3}\left(\frac{gt^2}{2x}\right)^2 - \ldots + (-)^n\frac{\Omega_n}{1.3\ldots(2n-1)}\left(\frac{gt^2}{2x}\right)^n + \ldots,$$

where

$$\Omega_n = \sum_{\lambda=1}^{\infty}(-)^\lambda\{n, \lambda\}\cos(n+1)\phi_\lambda\sin^{n+1}\phi_\lambda + \begin{cases}0, \text{ if } n \text{ is even,}\\ (-1)^{\frac{1}{2}(n+1)}, \text{ if } n \text{ is odd.}\end{cases}$$

The calculations were performed for the three values $\frac{1}{2}$, 1, and ∞ of h/x, the latter serving as a partial check on the accuracy of the work. The series for Ω_n converges very slowly if h/x is taken much less than $\frac{1}{2}$, while the final series for η converges slowly when t is large. It was found possible to take values of $t(g/2x)^{\frac{1}{2}}$ up to 4, but to go much further would necessitate not only the taking of more terms of each series, but also the use of more figures in the logarithms at every stage. The calculation of $\{n, \lambda\}$ was carried out by repeated application of the formula

$$\{n+1, \lambda\} = \{n+1, \lambda-1\}+\{n, \lambda\}+\{n, \lambda-1\}.$$

The values used corresponded roughly to $n + \lambda \leqq 25$, the value of $\{10, 10\}$ being checked independently.

The following table gives the numbers as they actually came out in calculation :—

$\pi x\eta/Q$.

$t(g/2x)^{\frac{1}{2}}$.	$h = \infty$.	$h = x$.	$h = \frac{1}{2}x$.	$t(g/2x)^{\frac{1}{2}}$.	$h = \infty$.	$h = x$.	$h = \frac{1}{2}x$.
1	0·93	1·13	0·79	2·75	−3·54	−1·58	−16·66
1·25	1·31	1·59	0·99	3	−3·23	−0·05	−26·26
1·5	1·55	1·96	0·84	3·25	−0·99	5·92	
1·75	1·42	1·97	−0·19	3·5	2·52	11·44	
2	0·70	1·47	−2·45	3·75	3·48	17·04	
2·25	−0·64	0·26	−6·40	4	3·4	29	
2·5	−3·31	−1·06	−12·03				

The comparison with Lamb's results shows that the numbers in the first column are probably accurate to 2 per cent., but that for $t(g/2x)^{\frac{1}{2}} = 4$ serious errors are introduced (by the use of four-figure logarithms). The figure below shows the rise of the surface when $x = \frac{1}{2}g$ for values of t from 0 to 3·5, taking $Q = \pi x/10$.

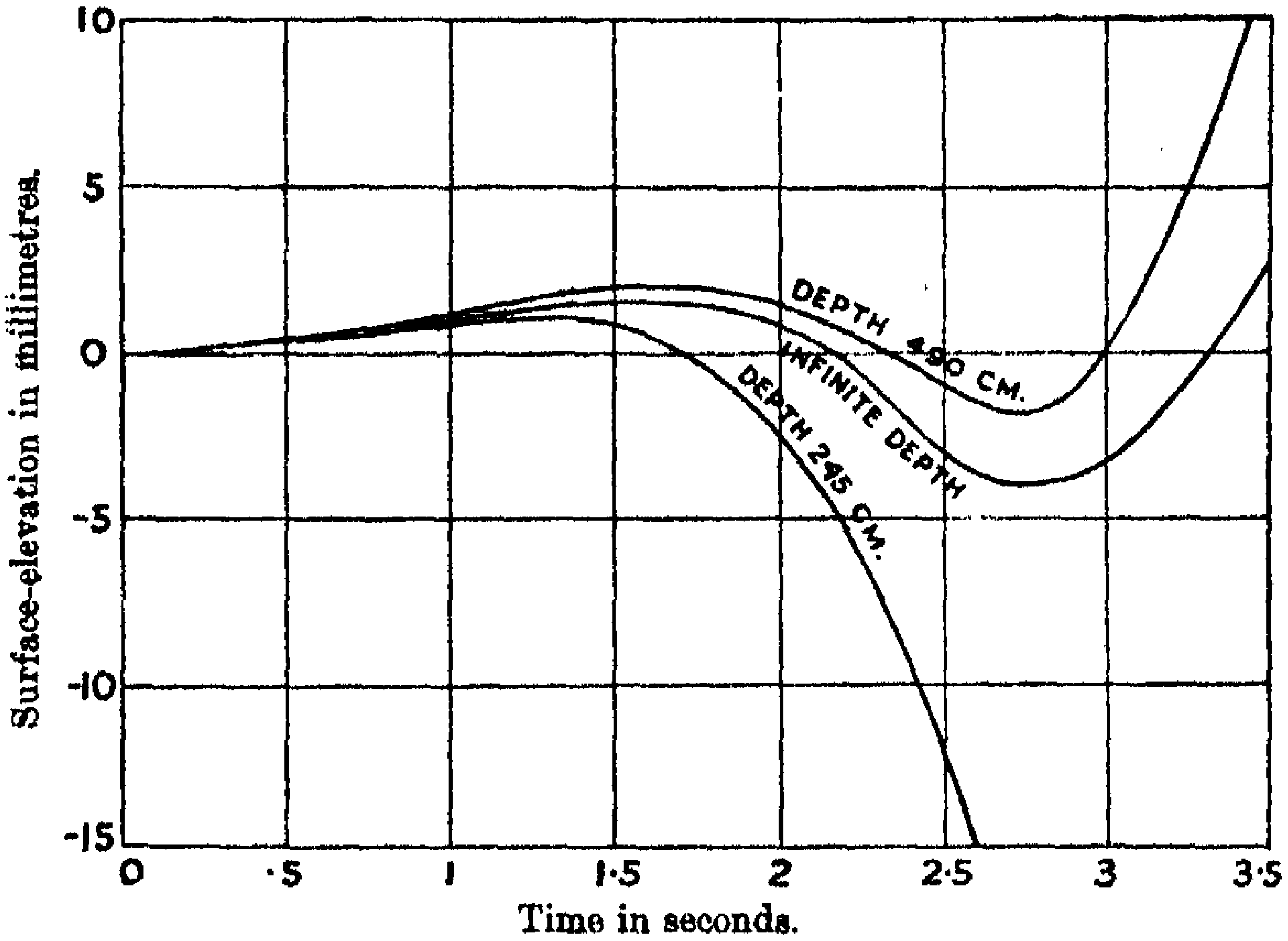

Fig. 1.—Surface-elevation at a fixed position at various times. $x = 490$ cm., initial area of fluid heaped up 154 sq. cm.

For depth 490 cm. a tidal wave of velocity $(gh)^{\frac{1}{2}}$ would arrive from the origin in 0·707 seconds, and for depth 245 cm. in one second. The peculiarities of very shallow water propagation have evidently not begun to appear for $h = \frac{1}{2}x$: when h is very small we should have nearly non-dispersive propagation with velocity $(gh)^{\frac{1}{2}}$. The surface-elevation at a given time is profoundly altered by making the depth finite, and seems to tend to lose its periodic character. It is remarkable that when $h = x$ the fluid actually begins to rise more quickly than when $h = \infty$. This is easily explained by means of Lord Rayleigh's formula* for the first term in η in ascending powers of t. Regarding h as the only variable, the coefficient of t^2 is proportional to $\theta^2 \cosh \theta / \sinh^2 \theta$, where $\theta = \pi x / 2h$. Its progress as a function of h is shown in fig. 2.

3. *Wave Motion in Heavy Compressible Fluid.*

There are two main cases of wave motion in fluid, namely, when the fluid starts to move from rest in a given configuration, and when it is set in motion by given impulses. The former problem presents features of some difficulty. In discussing it it is usual to assume that the fluid is incompressible, in which case the solution is known. It is, however, necessary to postulate a certain initial distribution of pressure throughout the fluid, which may be explained by saying that pressure is transmitted instantaneously in an incompressible fluid. No insight into the process of transmission is gained in this way, as the course of the infinitely quick redistribution of pressure cannot be followed mathematically. The assumption of absolute incompressibility also makes any specification of the initial configuration indeterminate; for it is evident that a homogeneous incompressible fluid only appears to be disturbed when its free surface is ruffled, so that all initial disturbances have to be described in terms of the elevation of the free surface.

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* Lord Rayleigh, 'Phil. Mag.' [6], 1909, vol. 18, p. 4.

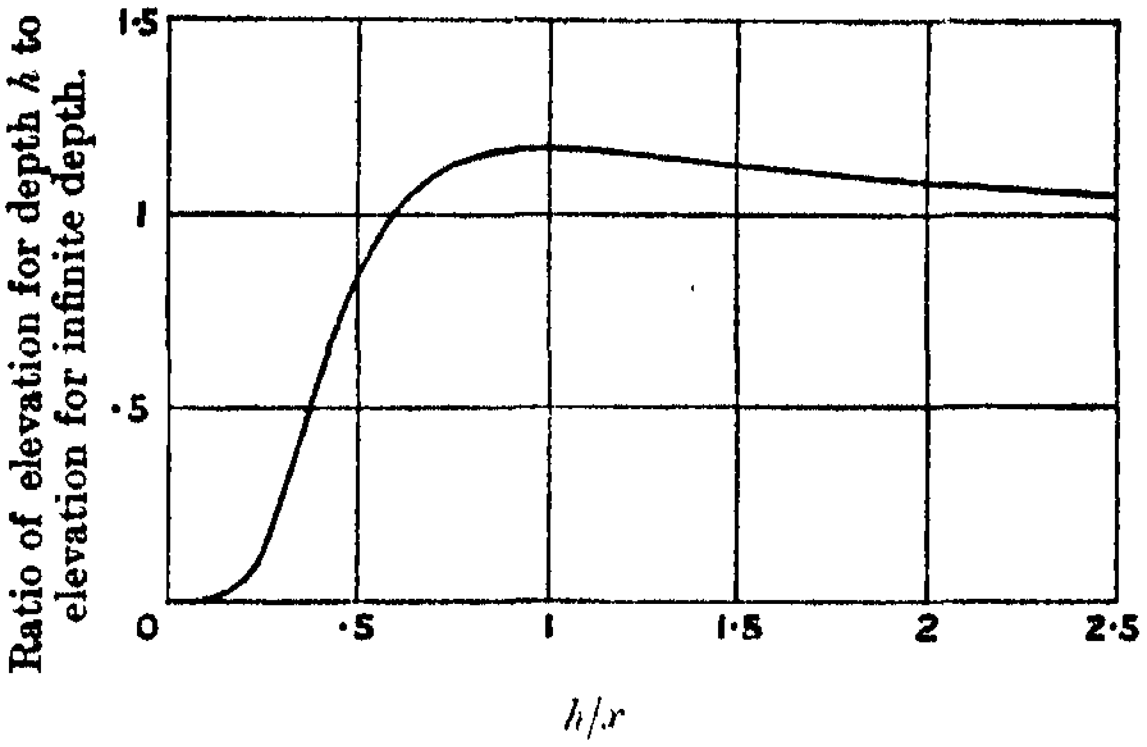

FIG. 2.—Elevation at a fixed distance x from the origin, and for a fixed small time t, expressed as a function of the depth h of the fluid.

The most natural way out of these difficulties seemed to the writer to be to consider, in the first place, a compressible fluid, and afterwards to pass to the limit when the compressibility is zero. A sufficient account of the matter will be given by the assumption p = constant + $a^2\rho$ of the previous paper; an incompressible fluid appears in the limit when a is infinite.

The essential features are illustrated well enough in two dimensions, which is the only case that will be considered. It has been found possible to obtain a result corresponding to very general initial conditions; in specialising the formulæ no attention has been paid to restrictions of a functional kind necessary to secure the validity of the theorems used.

For a finite constant depth h of fluid the immediate conditions of the problem are:—

(i) The differential equation

$$\frac{\partial^2\phi}{\partial t^2} = a^2\left(\frac{\partial^2\phi}{\partial x^2}+\frac{\partial^2\phi}{\partial y^2}+2\gamma\frac{\partial\phi}{\partial y}\right), \quad \text{where} \quad \gamma = g/2a^2; \tag{1}$$

(ii) The condition at the free surface,

$$\partial^2\phi/\partial t^2 = g\partial\phi/\partial y \quad \text{when} \quad y=0;$$

(iii) The condition

$$\partial\phi/\partial y = 0 \quad \text{when} \quad y = h;$$

(iv) The condition of initial rest,

$$\phi = 0 \quad \text{when} \quad t = 0.$$

The surface elevation at time t is $\eta = g^{-1}(\partial\phi/\partial t)_{y=0}$. In the present case we have to specify not only η, but also the *state of every element of fluid* at time $t = 0$. Since $\int\rho^{-1}dp = \partial\phi/\partial t + gy$, this is done by fixing the initial value of $\partial\phi/\partial t$ at every point; the initial value of η then follows as a necessary consequence. Let us therefore take as the last condition

$$\text{(v)} \qquad \frac{e^{\gamma y}}{g}\left(\frac{\partial\phi}{\partial t}\right)_{t=0} = \theta(x, y),$$

where $\theta(x, y)$ is an arbitrary function of x and y.

The suitable particular solutions of (i) to (iv) have already been given.* Their general type is given by

$$\phi e^{\gamma y} = (Ae^{\mu y} + Be^{-\mu y})\frac{\sin\sigma t}{\sigma}\cos kx,$$

where
$$\sigma^2/a^2 = k^2 - \mu^2 + \gamma^2,$$

or by
$$\phi e^{\gamma y} = (A\cos\nu y + B\sin\nu y)\frac{\sin\sigma t}{\sigma}\cos kx,$$

where
$$\sigma^2/a^2 = k^2 + \nu^2 + \gamma^2.$$

We may refer to these briefly as the μ and ν solutions respectively. The admissible values of μ and ν are given by the equations

$$\mu\coth\mu h = \gamma(k^2 + \mu^2 - \gamma^2)/(k^2 - \mu^2 + \gamma^2)$$

and
$$\nu\cot\nu h = \gamma(k^2 - \nu^2 - \gamma^2)/(k^2 + \nu^2 + \gamma^2).$$

respectively. The value of ν may, of course, be regarded as a purely imaginary value of μ. It does not seem easy to show directly that the above equation for μ has no complex roots of the form $a + ib$, but this can be shown by general considerations. For, if we assimilate the fluid to a dynamical system, and consider the modes of vibration involving x in the connexion $\cos kx$, the corresponding values of σ are purely real, or at most purely imaginary; and, since $\sigma^2/a^2 = k^2 - \mu^2 + \gamma^2$, the same is true of μ.

It is remarkable that Lord Kelvin's particular solutions for deep incompressible fluid,† as well as the normal Cauchy-Poisson solution, apply equally to the present ideal fluid. They are not, however, general enough for our present purpose, which is to satisfy the fifth condition of the problem as well as the first four.

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* P. 355 of the previous paper.

† Lord Kelvin, 'Phil. Mag.' [6], 1907, vol. 13, p. 1; 'Collected Papers,' vol. 4.

4. *Compressible Fluid, Infinite Depth.*

When k tends to infinity there is always the root $\mu = \gamma$, and also the root $\mu = k - \gamma$ if $k > \gamma$. The former gives $\phi = \cos kx \sin kat$, and corresponds to sound-waves propagated horizontally, but it will not be required here. The root $\mu = k - \gamma$ gives $\sigma^2 = gk$. The values of ν become heaped more and more together, and in the limit ν can take any value. The fundamental ν-solution can be written in the form

$$\frac{\phi e^{\gamma y}}{g} = \{2\nu\gamma \cos \nu y - (k^2 + \nu^2 - \gamma^2) \sin \nu y\} \frac{\sin \sigma t}{\sigma} \cos k (x - \xi),$$

where
$$\sigma^2 = a^2(k^2 + \nu^2 + \gamma^2). \tag{2}$$

It is to be expected that on generalising these solutions to fit the condition (v) we should obtain a solution in the form of a ν-integral, with an extra term corresponding to the μ-root when $k > \gamma$. In fact, the solution satisfying the condition (v) is

$$\frac{\pi\phi e^{\gamma y}}{g} = \frac{2}{\pi} \int_0^\infty d\nu \int_0^\infty \mathrm{A} \frac{\sin \sigma t}{\sigma} \frac{\{2\nu\gamma \cos \nu y - (k^2 + \nu^2 - \gamma^2) \sin \nu y\}}{(k^2 + \nu^2 - \gamma^2)^2 + 4\nu^2\gamma^2} \, dk$$
$$+ 2\gamma \int_\gamma^\infty \mathrm{B} \frac{k - \gamma}{k} \frac{\sin (gk)^{\frac{1}{2}} t}{(gk)^{\frac{1}{2}}} e^{-(k-\gamma)y} \, dk, \tag{3}$$

where*

$$\left.\begin{aligned} \mathrm{A} &= \int_{-\infty}^\infty \int_0^\infty \cos k (x - \xi) \{2\nu\gamma \cos \nu\eta - (k^2 + \nu^2 - \gamma^2) \sin \nu\eta\} \, \theta(\xi, \eta) \, d\xi \, d\eta, \\ \mathrm{B} &= \int_{-\infty}^\infty \int_0^\infty \cos k (x - \xi) \, e^{-(k-\gamma)\eta} \, \theta(\xi, \eta) \, d\xi \, d\eta. \end{aligned}\right\} \tag{4}$$

In order to verify this we have to prove that

$$\pi\theta(x, y) = \frac{2}{\pi} \int_0^\infty d\nu \int_0^\infty \mathrm{A} \frac{2\nu\gamma \cos \nu y - (k^2 + \nu^2 - \gamma^2) \sin \nu y}{(k^2 + \nu^2 - \gamma^2)^2 + 4\nu^2\gamma^2} \, dk$$
$$+ 2\gamma \int_\gamma^\infty \mathrm{B} \frac{k - \gamma}{k} e^{-(k-\gamma)y} \, dk.$$

The proof depends on a theorem of Orr,† who has given a very valuable extension of Fourier's theorem of the type required in this problem. Recalling Fourier's integral theorem in the form

$$\pi\theta(x, y) = \int_0^\infty dk \int_{-\infty}^\infty \cos k (x - \xi) \, \phi(\xi, y) \, d\xi,$$

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* The symbol η is here used in a new sense.

† W. M'F. Orr, "Extensions of Fourier's and the Bessel-Fourier Theorems," 'Royal Irish Acad. Proc.,' A, 1909, vol. 27, pp. 207—209.

we see that we have to prove that

$$\theta(\xi, y) = \frac{2}{\pi}\int_0^\infty \frac{2\nu\gamma\cos\nu y - (k^2+\nu^2-\gamma^2)\sin\nu y}{(k^2+\nu^2-\gamma^2)^2+4\nu^2\gamma^2}\,d\nu$$
$$\int_0^\infty \{2\nu\gamma\cos\nu\eta - (k^2+\nu^2-\gamma^2)\sin\nu\eta\}\,\theta(\xi,\eta)\,d\eta \qquad (5)$$

for $k<\gamma$, and that for $k<\gamma$ the term

$$2\gamma\frac{k-\gamma}{k}e^{-(k-\gamma)y}\int_0^\infty e^{-(k-\gamma)\eta}\theta(\xi,\eta)\,d\eta \qquad (6)$$

must be added on the right-hand side.

The result (5) is a case of Orr's theorem, allowing for the difference in notation; the condition that the roots of $C(\lambda)+iS(\lambda)=0$ should have negative imaginary parts reducing to the condition $k<\gamma$. The root $\lambda = i(k-\gamma)$, which in our notation is $\mu = i\nu = -(k-\gamma)$, gives rise, when $k>\gamma$, to a pole inside the contour used in Orr's proof. The residue of this pole is easily shown to cause the addition (6) to the right-hand side of (5).

Now let us confine the initial disturbance to the neighbourhood of the point $(0, u)$ within the fluid. Thus $\theta(x, y)$ is sensible only near this point, and we shall make it of such a magnitude that the double integral $\iint\theta(x, y)\,dx\,dy$ has the finite value $1/2\gamma = a^2/g$. The solution becomes

$$\frac{\pi\phi e^{\gamma y}}{g} =$$
$$\frac{1}{\pi\gamma}\int_0^\infty d\nu\int_0^\infty \frac{\{2\nu\gamma\cos\nu u-(k^2+\nu^2-\gamma^2)\sin\nu u\}\{2\nu\gamma\cos\nu y-(k^2+\nu^2-\gamma^2)\sin\nu y\}}{(k^2+\nu^2-\gamma^2)^2+4\nu^2\gamma^2}$$
$$\frac{\sin\sigma t}{\sigma}\cos kx\,dk + \int_\gamma^\infty\frac{k-\gamma}{k}e^{-(k-\gamma)(u+y)}\frac{\sin(gk)^{\frac{1}{2}}t}{(gk)^{\frac{1}{2}}}\cos kx\,dk. \qquad (7)$$

We can now pass to the limit when a is infinite, so that γ tends to zero. The first step is to prove that the first integral becomes indefinitely small. The most important term is

$$\frac{1}{\pi\gamma}\int_0^\infty \sin\nu u\sin\nu y\,d\nu\int_0^\infty\frac{\sin(k^2+\nu^2)^{\frac{1}{2}}at}{a(k^2+\nu^2)^{\frac{1}{2}}}\cos kx\,dk.$$

The integral with respect to k has the value*

$$\frac{\pi}{2a}J_0\{\nu(a^2t^2-x^2)^{\frac{1}{2}}\},$$

if $at>x$, and we may further replace it by its approximate value $\frac{\pi}{2a}J_0(\nu at)$;

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* Nielsen, 'Cylinderfunktionen,' p. 255.

or $\frac{1}{2}\left(\frac{\pi}{\nu a^3 t}\right)^{\frac{1}{2}}(\cos \nu at+\sin \nu at)$, since a is large. Hence the double integral becomes

$$\frac{1}{g}\left(\frac{a}{\pi t}\right)^{\frac{1}{2}}\int_0^\infty \frac{\sin \nu u \sin \nu y\,(\cos \nu at+\sin \nu at)}{\sqrt{\nu}}\,d\nu.$$

Now when λ is positive, $\int_0^\infty \begin{matrix}\cos\\ \sin\end{matrix}\lambda\nu \frac{d\nu}{\sqrt{\nu}}=\left(\frac{\pi}{2\lambda}\right)^{\frac{1}{2}}$, so that, expressing the products of trigonometrical functions as sums, we find that the above expression becomes

$$\frac{1}{4g}\left(\frac{2a}{t}\right)^{\frac{1}{2}}\{(at+y-u)^{-\frac{1}{2}}+(at-y+u)^{-\frac{1}{2}}-(at+y+u)^{-\frac{1}{2}}-(at-y-u)^{-\frac{1}{2}}\},$$

which tends to zero as a tends to infinity. The rest of the first integral is easily shown to vanish for $a=\infty$.

Hence, in the limit when the compressibility of the fluid is zero we have

$$\phi=\frac{g}{\pi}\int_0^\infty e^{-k(u+y)}\frac{\sin (gk)^{\frac{1}{2}}t}{(gk)^{\frac{1}{2}}}\cos kx\,dk, \tag{8}$$

which reduces to the integral solution of the Cauchy-Poisson problem when $u=0$.

Returning to the equation (7), the first term may be described roughly as the spreading out of the initial pressure by sound-waves in the fluid, and the second as the Cauchy-Poisson term predominating after a time. It is interesting to verify that we are really dealing, for finite values of a, with a case of finite propagation, that is, to find the points of non-uniform convergence of the first integral in (7). As we are only concerned with large values of k and ν, we can just as well consider the integral

$$\int_0^\infty \sin \nu u \sin \nu y\,d\nu \int_0^\infty \frac{\sin \sigma t}{\sigma}\cos kx\,dk, \text{ where } \sigma^2=a^2(k^2+\nu^2+\gamma^2).$$

The integral with respect to k is zero* when $at<x$, and when $at>x$ its value is $\frac{\pi}{2a}J_0\{(\nu^2+\gamma^2)^{\frac{1}{2}}(a^2t^2-x^2)^{\frac{1}{2}}\}$. Thus the convergence of the double integral is of the same kind as that of the single integral

$$\int^\infty \nu^{-\frac{1}{2}}\sin \nu u \sin \nu y\,\{\cos \nu(a^2t^2-x^2)^{\frac{1}{2}}+\sin \nu(a^2t^2-x^2)^{\frac{1}{2}}\}\,d\nu;$$

and this latter integral is non-uniformly convergent near the points where $(a^2t^2-x^2)^{\frac{1}{2}}=\pm y\pm u$, *i.e.* where $a^2t^2=x^2+(y\pm u)^2$. Hence one set of points of non-uniform convergence occurs where a sound-wave starting from $(0, u)$ with velocity a arrives after a time t has elapsed, as we should expect. The other set arises from the quasi-reflection of the disturbance at the free surface.

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* Nielsen, p. 252.

5. *Finite Depth, Small Compressibility.*

It is possible to give a formal solution of the problem when the depth of the fluid is finite, by using an extension of Fourier's series given in the latter part of Orr's paper. We shall find it convenient to express all the solutions in the exponential form by writing $\mu = i\nu$. The fundamental solution is

$$\frac{\phi e^{\gamma y}}{g} = \{\mathrm{P}e^{\mu y} + \mathrm{Q}e^{-\mu y}\}\frac{\sin\sigma t}{\sigma}\cos k(x-\xi),$$

where

$$\sigma^2 = a^2(k^2-\mu^2+\gamma^2), \tag{9}$$

and the conditions satisfied by P and Q are

$$\mathrm{P}\{k^2-(\mu-\gamma)^2\} + \mathrm{Q}\{k^2-(\mu+\gamma)^2\} = 0$$

and

$$\mathrm{P}(\mu-\gamma)e^{\mu h} - \mathrm{Q}(\mu+\gamma)e^{-\mu h} = 0.$$

Writing

$$\left.\begin{aligned} \alpha(\mu, y) &\equiv e^{-\mu(h-y)}(-\mu-\gamma) - e^{\mu(h-y)}(\mu-\gamma) \\ \beta(\mu, u) &\equiv e^{\mu u}\{k^2-(\mu+\gamma)^2\} - e^{-\mu u}\{k^2-(\mu-\gamma)^2\} \\ \zeta(\mu) &\equiv e^{\mu h}(\mu-\gamma)\{k^2-(\mu+\gamma)^2\} + e^{-\mu h}(\mu+\gamma)\{k^2-(\mu-\gamma)^2\} \end{aligned}\right\}, \tag{10}$$

the solution for finite depth is

$$-\frac{\pi\phi e^{\gamma y}}{g} = \Sigma\alpha(\mu, y)\int_0^\infty \frac{1}{\zeta'(\mu)}\frac{\sin\sigma t}{\sigma}\,dk\int_{-\infty}^\infty \cos k(x-\xi)\,d\xi\int_0^h \beta(\mu, u)\,\theta(\xi, u)\,du. \tag{11}$$

The summation is extended over the roots of $\zeta(\mu) = 0$, which are precisely the quantities μ and ν already employed. The process of verifying this solution is the same as before. Using Fourier's integral theorem, we find that we have to prove that

$$-\theta(\xi, y) = \Sigma\frac{\alpha(\mu, y)}{\zeta'(\mu)}\int_0^h \beta(\mu, u)\,\theta(\xi, u)\,du$$

for $0 < y < h$. This is included in Orr's result.*

The case which is easiest to interpret is that of a concentrated disturbance in nearly incompressible fluid. When γ is small it is superfluous to attend to the restriction that $k > \gamma$, and it is easy to see that there is one μ-root nearly equal to k. Its approximate value is $k - \gamma\tanh kh$, giving $\sigma^2 = gk\tanh kh$ nearly. As before, the initial disturbance will be located near $(0, u)$ and such that $\iint\theta(x, y)\,dx\,dy$ is equal to a^2/g, in this case a large quantity. The part of ϕ corresponding to the above root is found to be

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* W. M'F. Orr, *loc. cit.*, p. 238. It must be borne in mind that only positive values of μ and ν are considered here, while Orr considers all the roots.

$$\frac{g}{\pi}\int_0^\infty \frac{\cosh k(h-u)\cosh k(h-y)}{\cosh^2 kh}\,\frac{\sin (gk\tanh kh)^{\frac{1}{2}}t}{(gk\tanh kh)^{\frac{1}{2}}}\cos kx\,dk. \tag{12}$$

The other roots tend to $\mu h = i(n+\frac{1}{2})\pi$, or $\nu h = (n+\frac{1}{2})\pi$, where $n = 0, 1, 2 \ldots$, the part of ϕ belonging to a particular one being

$$\frac{2a}{\pi h}\int_0^\infty \sin \nu u \sin \nu y\,\frac{\sin (k^2+\nu^2)^{\frac{1}{2}}at}{(k^2+\nu^2)^{\frac{1}{2}}}\cos kx\,dk,$$

that is

$$\frac{1}{h}\left(\frac{a}{\pi t}\right)^{\frac{1}{2}}\nu^{-\frac{1}{2}}\sin \nu u \sin \nu y\,(\cos \nu at + \sin \nu at). \tag{13}$$

The mere fact of making a large is not enough to make the aggregate of terms (13) negligible. In reality, they become large and quickly oscillatory for finite values of t. In a number of important cases, however, they are small and the velocity-potential is given by (12). They do not appear, for example, when either the source of disturbance or the point of observation is on the free surface of the fluid. The terms also become negligible when t is large, while the expression (12) increases without limit. This latter circumstance is, of course, due to the supposition that the initial elevation is confined to an infinitely small region near the origin, and would disappear on a more natural assumption.

On the Devitrification of Silica Glass.

By Sir WILLIAM CROOKES, O.M., For. Sec. R.S.

(Received February 15,—Read March 7, 1912.)

The use of apparatus blown and worked from melted quartz is now almost universal in chemical laboratories, especially where temperatures are required above the heat at which glass softens.

When working at fairly high temperatures, I was inconvenienced by the leakage of air through silica glass.* The apparatus (fig. 1) was in the form of a perfectly clear and transparent tube, 1 cm. diameter and 20 cm. long, with a bulb 2½ cm. diameter blown on the end. The other end of the silica tube was drawn out for connecting with the pump and sealing. It was exhausted to a high vacuum and heated to near redness along its whole length to remove any gas that might be condensed on the walls—it was then sealed off.

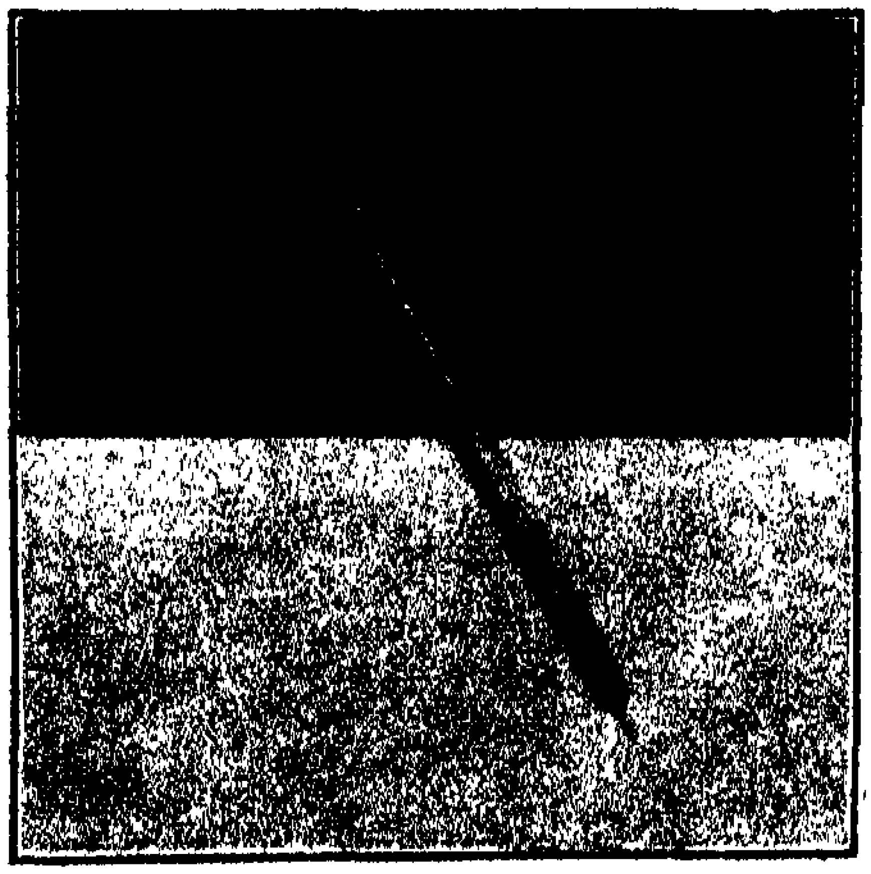

FIG. 1.

The tube was placed bulb uppermost in an electric resistance furnace in such a position that the bulb would be at the point of greatest heat, the lower part of the tube remaining comparatively cool; it was kept at a temperature of 1300° for 20 hours, at the end of which time the silica tube was removed from the furnace. The long continued high temperature caused the bulb and the upper part of the tube to devitrify, and become white and translucent like frosted glass. The sealed-off end was carefully opened, and it was apparent that the inrush of air was by no means so strong as it would have been had the vacuum been as perfect as it was when the tube was sealed up.

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* Jaquerod and Perrot have shown that fused silica is permeable to helium and hydrogen at a low red heat ('Comptes Rendus,' Nov., 1904, vol. 139, p. 789; and Jan. 1907, vol. 144, p. 135).

This looked as if there had been a considerable amount of leakage through the devitrified bulb, and I tried a test experiment. The tube was again attached to the Sprengel pump, and exhausted to as high a point as possible. During the progress of exhaustion, when the pump was rattling with the characteristic sound of a high vacuum, a large and powerful Bunsen flame was used to heat the bulb. Not the least difference in the sound could be distinguished. When the vacuum was at its highest the tube was sealed off; it was put into the electric furnace, and kept at a temperature of 1300° for 11 hours. After cooling, the end of the tube was broken off under mercury. The mercury rose, but did not fill the bulb. The amount that entered was measured, and found to be 17·75 c.c. Afterwards the tube and bulb were completely filled with mercury, the whole again measured, and the capacity of the tube and bulb was found to be 19·25 c.c., showing that 1·5 c.c. of gas, or 7·79 per cent. of the tube's capacity, had leaked through the devitrified silica in 11 hours at 1300°.

To ascertain if air would leak through the devitrified silica at the ordinary temperature a facsimile of tube and bulb was made in glass, and the two tubes were simultaneously exhausted on the pump. They were both heated, allowed to cool, and sealed off at the same time. The silica and glass tubes were put in the balance case and kept there for some time. When they were both at uniform temperature the silica tube was weighed. The tube and weights not being moved in the meantime, weighings were taken hourly, the balance being untouched during the intervals. In 18 hours the weight increased 0·048 grain.

After the silica and glass tubes had been at rest for some days, they were opened simultaneously under mercury. The glass tube filled at once, only a microscopic bubble of air remained at the top. The silica tube, on the contrary, only partially filled, and, on measuring the mercury that entered, it amounted to 10·15 c.c., the capacity of the tube being 19 c.c. Therefore, in a few days, air to the amount of 46·58 per cent. of the total capacity of the apparatus had leaked in.

A micro-photograph was taken of the surface of the devitrified silica bulb (fig. 2). It showed a surface cracked all over into the appearance of cells, and, on closer examination, many of the cells showed decided hexagonal outline.

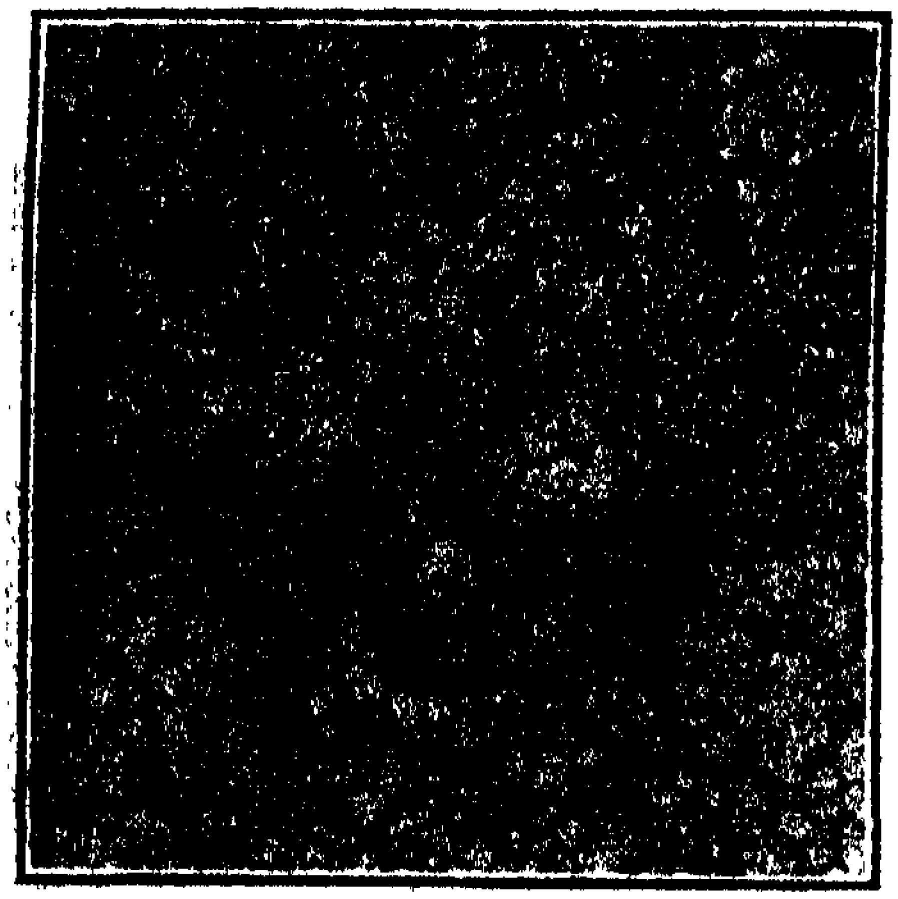

FIG. 2.

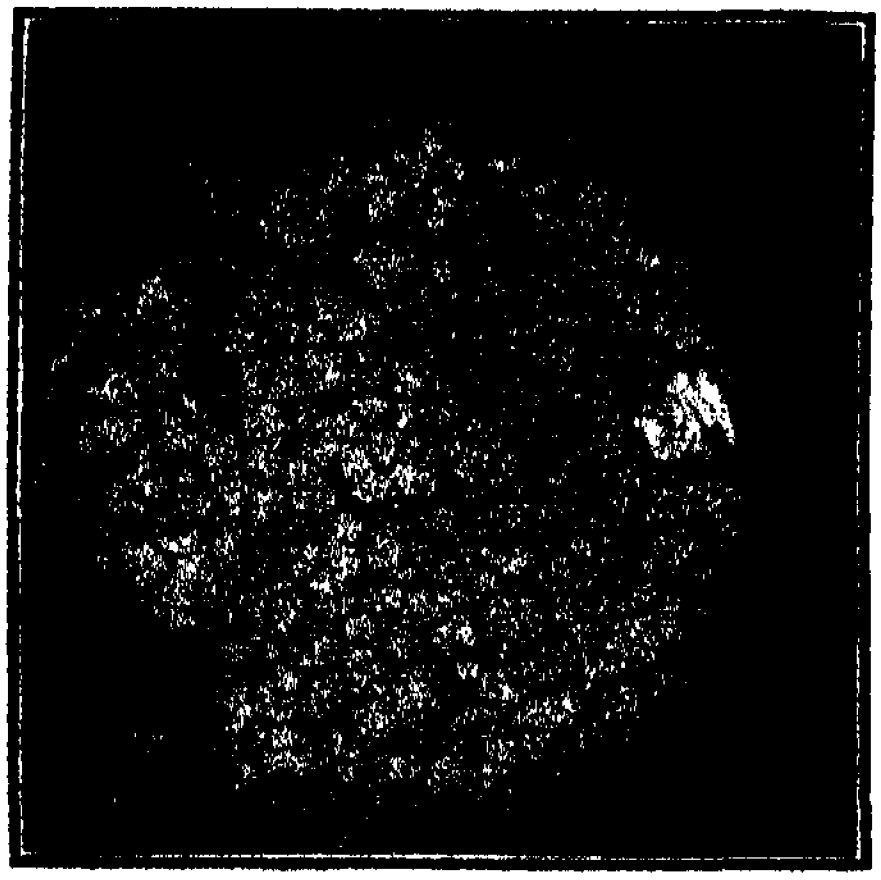

FIG. 3.

I observed a similar appearance a few years ago, when a silica dish, originally clear and transparent as glass, was used for evaporating down about 100 mgrm. of pure radium bromide. Patches appeared on the bottom having a dull, roughened appearance, and, on examination under the microscope, the appearance was very similar to the surface of the devitrified silica bulb just described (fig. 3). The appearances are so alike that it is legitimate to assume that the same cause had been at work, and that devitrification of the surface is produced both by exposure to a very high and long continued temperature and to the contact with a radium salt at a temperature of boiling water. I have not seen this effect on the surface of glass or silica bottles in which radium salts have been kept in the cold for some years.

Experimental Work on a New Standard of Light.

By W. A. HARWOOD and J. E. PETAVEL, F.R.S.

(Received January 10, 1911,—Read March 21, 1912.)

The competition between flame and incandescent standards of light, which has existed almost since the necessity for a standard began to be realised, has resolved itself for the time being into a compromise, so that, while Europe continues to employ the flame standard and America the electric glow-lamp, the relation of these two has been accurately determined, and they are now expressible in terms of the accepted International standard candle.* This state of affairs, however, can hardly be considered as final, and effort has not altogether ceased to be directed towards finding some standard free from the defects of those at present in use. The following is an account of the results of an examination of an incandescent standard proposed some years ago.†

In bringing forward the original proposal, a review of the state of the subject led to the following conclusions:—

(1) The Violle molten platinum standard is satisfactory as an absolute standard of reference.

(2) The flame standards are the most convenient for general use, and are of sufficient accuracy for commercial purposes.

(3) The secondary standard, intended to serve as a go-between from the absolute to the commercial standards, are in the least satisfactory state of the three. The sets of Fleming large-bulb glow-lamps, which are now so largely used, are subject to a gradual decay and to the multiplication of photometric errors by successive inter-comparison.

The suggested new standard was intended to fill the gap, by providing a single apparatus, which should be free from the above defects. The principle upon which it was based consisted in taking the quality of the radiation itself as the criterion by which the temperature of the radiator was regulated.

The sensitiveness and accuracy of the spectrophotometer and spectrobolometer proved to be insufficient for this purpose, and the analysis of the radiation was obtained by making use of the selective absorption of black fluorspar and water, the former of which transmits essentially radiation of long wave-length, to which the latter is nearly opaque.

The method used may be described as follows: The electric radiator consists of a wide strip of metal placed behind a water-cooled diaphragm. Two thermopiles, connected in opposition, are placed on the right and left of the axis of the photometer, and receive respectively the radiation passing through a plate of black fluorspar and through a water-trough. As the temperature of the radiating strip increases, the percentage of the total radiation which penetrates the water will increase, and the percentage which penetrates the fluorspar will decrease. At some temperature the two will be equal, and the electromotive force in the galvanometer circuit will therefore fall to zero. This zero point may be used to fix the standard temperature.

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* 'Phil. Mag.,' August, 1909, vol. 18, p. 263.

† 'Electrician,' April 10, 1903, vol. 50, p. 1012.

The choice of a suitable material for the radiator offered some difficulty. The emissivity of the oxides of the rare earths alters under prolonged heating, and only the metals of the platinum group will withstand exposure to air when at a high temperature. Iridium disintegrates rapidly at temperatures above 1600° C., a continuous stream of black smoke arising from the surface of the metal. The loss of weight measured on various occasions amounted to about 4 mgrm. per square centimetre per hour. The evaporation of platinum is about 10 times slower, but, unless the metal is chemically pure, a gradual change in the texture of the surface produces a variation in the intensity of the light emitted.

After a long series of experiments, chemically pure platinum was chosen as the radiating substance. The apparatus was first set up, and subjected to tests extending over several months. The experience thus gained resulted in the construction of a self-contained instrument, the cost of which was defrayed by the Government Grant Committee of the Royal Society.

The platinum strip, 7 × 1·2 cm. and about 0·05 mm. thick, was stretched between two water-cooled clips connected to a low-tension battery through a variable resistance. The strip was enclosed in a cylindrical water-cooled casing having three apertures. The light, passing through a diaphragm, was directed on the photometer head, and the radiation emitted from the other side of the same portion of the strip reached the two thermopiles, which were placed at 30° to the axis of the photometer.

Careful tests proved that, with suitable precautions, the variations in intensity of the light emitted by such an apparatus will not exceed ± 0·5 per cent., and in this respect the result of the work can be considered entirely successful. On the other hand, this form of standard is not portable, the intensity of the light emitted is low, its colour unsatisfactory, and, finally, much skill and care is required in the adjustment of the very sensitive thermo-electric circuit. From a practical point of view, these defects are probably sufficient to outweigh the advantage gained with regard to accuracy, and it is therefore thought unnecessary to give a detailed account of the experimental work.

The Kinetic Theory of a Gas Constituted of Spherically Symmetrical Molecules.

By S. CHAPMAN, M.Sc., Chief Assistant, Royal Observatory, Greenwich.

(Communicated by Sir J. Larmor, Sec. R.S. Received May 29,—
Read June 29, 1911.)

(Abstract.)

In order to extend Maxwell's later method of developing the dynamical theory of a gas* to cases other than that which he considered (viz., a gas whose molecules are point centres of repulsive force varying inversely as the fifth power of the distance), a knowledge of the velocity distribution function, in the disturbed state of the gas, is necessary. In this paper the simplest possible form is assumed for the function, consistent with the fulfilment of certain preliminary conditions. This form is

$$\left(\frac{hm}{\pi}\right)^{\frac{3}{2}} e^{-hm\Sigma(u-u_0)^2}\{1+\mathrm{F}(u-u_0, v-v_0, w-w_0)\},$$

where F is a polynomial, in the three variables indicated, of the third degree. The theory of viscosity and thermal conduction, in simple and mixed gases, is developed without assuming any property of the molecules beyond that of spherical symmetry.

Perhaps the most interesting result is the relation between the viscosity μ, the thermal conductivity ϑ, and the specific heat at constant volume, C_v, for a simple monatomic gas, viz.,

$$\vartheta = \tfrac{5}{2}\mu C_v.$$

Maxwell obtained this relation for a gas of the particular kind above mentioned, but it is here obtained without reference to the law of action between the molecules. Schwarze's experiments† on argon and helium show that the law is very closely followed in the case of these two gases (the only monatomic gases for which data are available); Meyer's formula, $\vartheta = 1{\cdot}60\mu C_v$, is widely departed from.

Others of the formulæ obtained are unmanageable in their general form, but have been worked out completely in the case of three special laws of action between the molecules; these are, that the molecules behave as (*a*) elastic spheres, (*b*) elastic spheres which attract one another, or (*c*) point

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* 'Phil. Trans.,' 1867 and 1879; or 'Scientific Papers,' vol. 2, pp. 23, 681.

† 'Ann. d. Phys.,' 1903, vol. 11, p. 303; 'Phys. Zeitschrift,' 1903, vol. 4, p. 229.

centres of repulsive or attractive force varying inversely as the nth power of the distance.

The assumed form of the velocity distribution function, however, is incomplete. Enskog* has shown that the function F must take the form of an infinite series, except in Maxwell's special case. On this account the numerical constants of the formulæ obtained may require to be modified by factors which in cases (*a*) and (*c*) are numerical only, and in other cases also depend on the temperature. The determination of these factors is extremely difficult, and is not effected in the paper; but the comparison of the formulæ, as they stand, with the experimental results appears to indicate that the errors of approximation are small.

Maxwell's theory of diffusion is also extended to the most general kind of monatomic gas; this part of the work is not affected by the assumption concerning F, which is not required in this part of the theory.

The comparison of the formulæ with experimental results tends to show that the second type of molecule considered, viz., an elastic sphere surrounded by a field of attractive force, gives, on the whole, the best representation of the behaviour of actual molecules, so far as concerns the three particular phenomena of gases here discussed.

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* 'Phys. Zeitschrift,' 1911, vol. 12, p. 58.

A Critical Study of Spectral Series. Part II.—*The* p *and* s *Sequences and the Atomic Volume Term.*

By W. M. Hicks, Sc.D., F.R.S.

(Received January 24,—Read March 7, 1912.)

(Abstract.)

This is a sequel to a paper on the same subject published in the 'Philosophical Transactions,' vol. 210 (1910). The sequences which give the principal and the sharp series are discussed as they occur in the second and third groups of the periodic table of the elements, and it is found that the sequences, or types of formulæ, which in the alkalies give the principal and sharp series, here give the sharp and principal. In order to prevent confusion the notation P and S sequence is changed to *p* and *s* sequence, the letters P, S, being reserved for principal and sharp series. Additional evidence is afforded to show that these sequences depend on the atomic volumes of elements in a quite definite way.

An attempt is made to allot the S and D series of europium and of radium. The spectrum of Eu affords evidence that the element fills the gap between Cd and Hg, and from the series formulæ of both elements regarded as functions of their atomic volumes probable values of their densities are obtained, viz., 12·58 for Eu and either 5·10 or 6·12 for Ra.

Further, the result obtained in Part I, that if the denominator of the *p* sequence be thrown into the form $m+1-W(1-m^{-1})+\mu-\alpha m^{-1}$ the ratio α/μ is a constant (0·21520 with uncertainty in the last two digits), is confirmed for elements of second and third groups. A comparison of denominators of corresponding orders of P series, and of these with those of S series, gives relations which can be used as tests for their proper allocation in doubtful cases. In consequence slight modifications are suggested in Paschen's lists of upper lines of HgP and CaP.

Two appendices are added, one dealing with the S and D series of Eu and Ra, the other giving lists of the S and P series lines treated of, with some historical notes.

An Optical Load-extension Indicator, together with some Diagrams Obtained therewith.

By Prof. W. E. DALBY, City and Guilds Engineering College.

(Communicated by Sir J. A. Ewing, K.C.B., F.R.S. Received January 20,—Read March 7, 1912.)

The object of this paper is to describe an instrument by means of which load-extension diagrams of different materials may be obtained with precision, and to show some of the diagrams obtained therewith.

The majority of machines for testing the strength of materials are fitted with apparatus for the purpose of obtaining automatically load-extension diagrams of the specimens tested. In a common form of the instrument the diagram is drawn by a pencil or tracing point on a sheet of paper wrapped round a drum. The pencil is constrained so that it is only free to move in a direction parallel to the axis of the drum. The instrument can be attached to the frame of the machine, or to a support external to the frame. The pencil receives a motion proportional to the extension of the specimen through the agency of a fine wire carried over guide pulleys to clips fixed at a definite distance apart on the specimen, whilst simultaneously the drum receives an angular displacement proportional to the load applied to the specimen by means of a wire led over guide pulleys and fastened to the jockey weight.

The load-extension diagram obtained in this way is not strictly the load-extension diagram of the specimen under test, because the real load on the specimen is the load apparently applied by the jockey weight *plus* the effect of the inertia of the jockey weight and the beam. Any rapid change of load on the specimen as at the yield point is not truly recorded on the diagram. There are other ways of making the apparatus, but the diagrams obtained are in general subject to errors due to the inertia of the beam or the parts of the recording gear; to errors due to friction and to stretching of the cord; to errors due to relative movement between the instrument and the specimen.

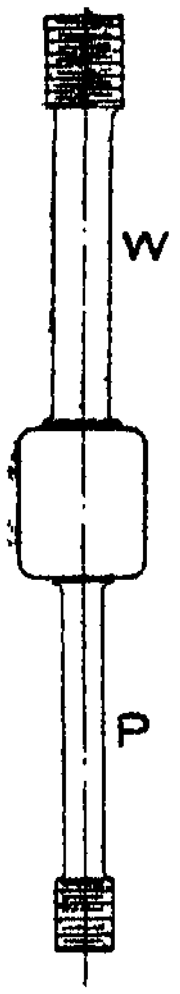

FIG. 1.—Weigh-bar and specimen in series.

The inertia effect of the beam and jockey weight is entirely eliminated by the use of a weighing bar placed in series with the specimen as indicated in fig. 1, where W represents the weigh-bar and P represents the specimen.

The load on the specimen is in this arrangement measured by the extension of the weigh-bar suitably magnified.

The cross-section of the weigh-bar must be so proportioned in relation to the cross-section of the specimen that the specimen breaks before the stress in the weigh-bar reaches the elastic limit of the material, in order that the straight line law between the load and extension of the weigh-bar may not be sensibly departed from before the specimen breaks. This condition limits the extension of a weigh-bar of 10 inches effective length to about two-hundredths of an inch.

The mechanical multiplication of the small extensions of the weigh-bar to the extent required to show them to a sufficiently large scale presents difficulties.

An instrument in which this mechanical multiplication was successfully accomplished was, however, designed by Sir Alexander Kennedy and the late Prof. Ashcroft, and an account of it by Sir Alexander Kennedy, together with some diagrams obtained, will be found in the discussion of a paper in the 'Proceedings of the Institution of Mechanical Engineers,' 1886, entitled "Autographic Test-recorders," by Mr. J. H. Wicksteed.

In the instrument designed by the author, the inertia of the beam is eliminated by the use of a weigh-bar, as in Prof. Kennedy and Prof. Ashcroft's instrument, but the magnification of the extension of the bar is done optically, and the diagram is obtained photographically, thus eliminating pencil and other sources of friction. The extension is measured at the axis of the bar, which is bored out to take the necessary apparatus, thus eliminating errors due to unequal extension and bending.

Description of the Instrument.—The instrument (fig. 2) consists of (*a*) a weigh-bar W; (*b*) the optical apparatus for magnifying the extension of the weigh-bar; (*c*) the optical apparatus for projecting the extension of the specimen on to the photographic plate, together with the mechanical apparatus connecting the mirror lever with the specimen; (*d*) the illuminating apparatus; (*e*) the camera.

A special feature of the instrument is that the camera, the optical apparatus and the illuminating apparatus are attached to the weigh-bar, and have no contact with the frame of the machine or with any support external to the frame, so that the diagram is unaffected by any straining action in the frame itself, or by any relative movement between the specimen and the frame.

A diagrammatic arrangement of the instrument is shown in figs. 2 and 3. The ends of the weigh-bar W are screwed, and it is bored out to take the optical apparatus for magnifying the extension.

A small concave mirror M is mounted on a frame carrying three hard steel points. The line joining the points 1 and 2 is the axis about which the mirror is free to turn. A light steel tube *t*, pointed at the lower end to rest in the cone formed at the bottom of the bar, and coned at the top to take the point 3 of the optical lever, is kept in position by the spring *s*, fig. 3.

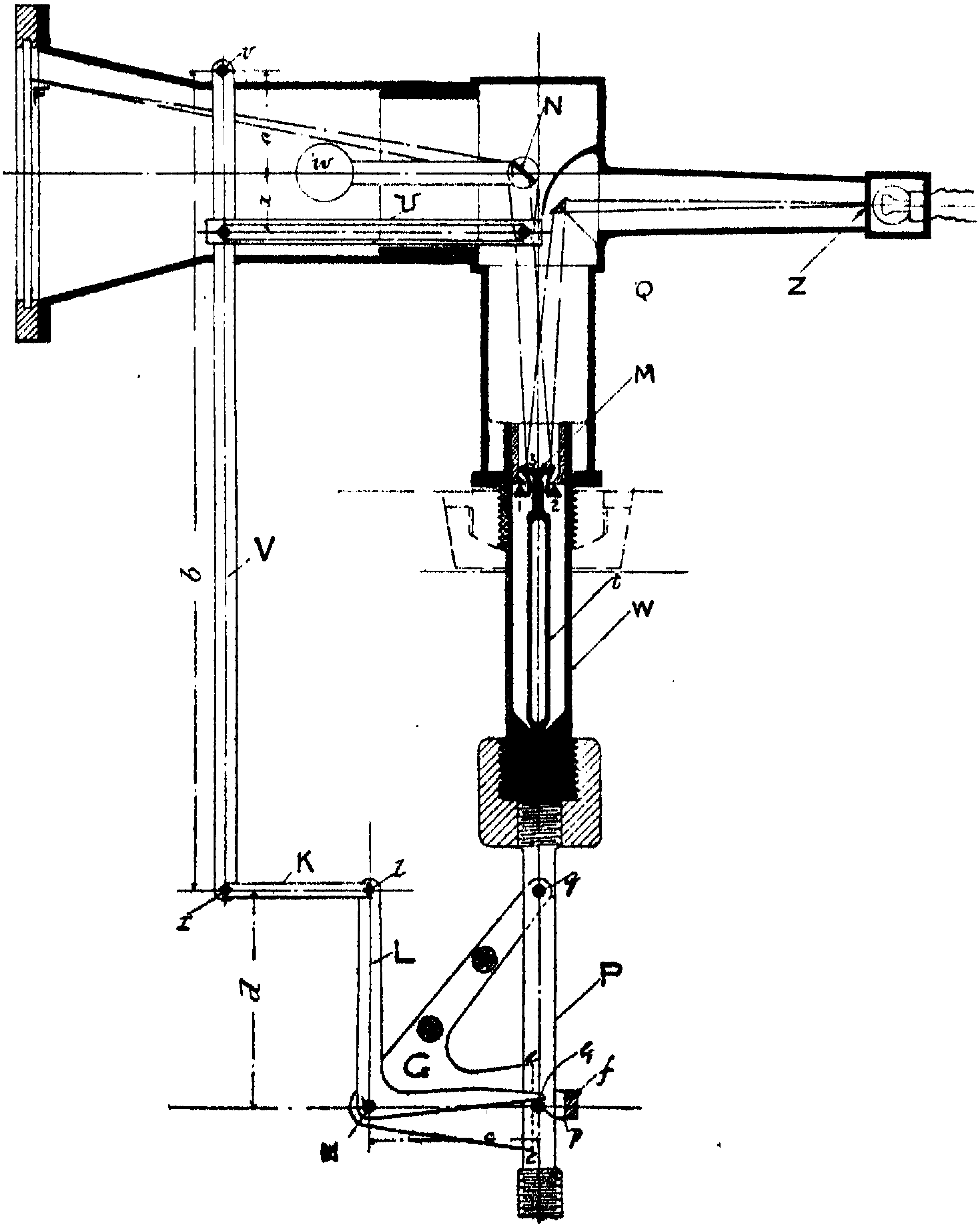

FIG. 2.—General arrangement of indicator in section.

The extension of the weigh-bar tilts the mirror M through an angle x/l, where x is the extension and l is the length of the arm of the optical lever.

A beam of light starting from the source Z is reflected by the fixed mirror Q on to the mirror M, from which it is reflected to the mirror N, and from N it is brought to a focus on the photographic plate F. The source of light Z and the focus at F are conjugate with respect to the mirror M.

It will be understood from this that the spot of light focussed on the plate moves horizontally across the plate as the weigh-bar extends. In the actual apparatus the dimensions are such that the spot moves 340 times the actual extension of the bar, so that an extension of 1/100 of an inch corresponds with a movement of the spot of 3·4 inches horizontally. This horizontal movement is proportional to the load actually applied to the specimen through the weigh-bar W.

The mirror N is carried on an axis placed at right angles to the axis 1 2 about which the mirror M turns.

The axis of N is connected to the specimen P by a linkage which ensures that the angular movement of N is proportional to the extension of the specimen P between the gauge points q and p.

The points of two steel screws, p, p (fig. 3), carried by a frame f, are forced into the specimen and are held in place as the diameter of the specimen contracts, by the spring of the frame f.

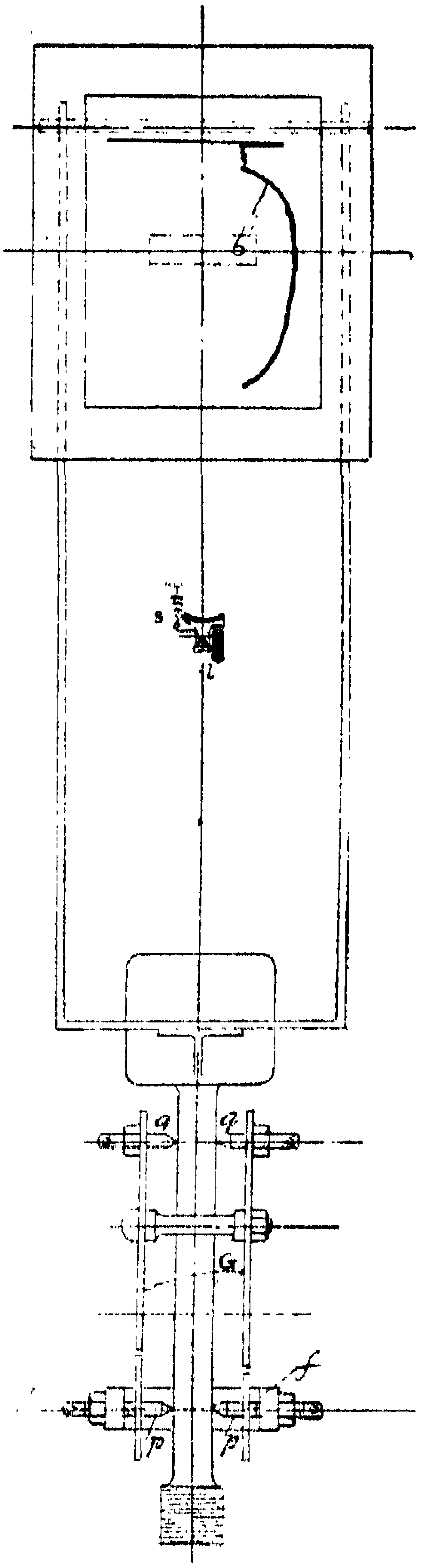

FIG. 3.—End elevation.

A frame G is attached by similar pointed screws, q, q, to the specimen at a parallel diameter 5 inches above the lower points, p, p, and the spring of the side plates of the frame maintains the points of q, q, in contact with the specimen as the diameter contracts. This frame G is free to turn about the axis qq, and it does so until its vertical edge *ee* (fig. 2) finds contact with the turned part of the lower screws, *p*, *p*, and contact is maintained by the weight of the frame itself.

Thus the lower frame *f*, carrying the pointed screws, *p*, *p*, is not directly connected with any other part; but the turned surfaces of the screws, *p*, *p*, near the point provide surfaces against which the vertical edges *ee* of the frame G rest.

The frame G is provided to carry an axis H for the bell-crank lever L so that, as the specimen extends, the axis H remains at a fixed distance *c* from the centre line of the specimen.

A bell-crank lever L is free to turn about the axis H. One arm rests on the pin *p* and follows it as the specimen extends, contact being maintained by the weight *w* above acting through the linkage, whilst the other arm is connected by a link K to the end of a hanging lever V which is free to turn about the axis *v*.

This hanging lever V is so long relatively to the displacement of its end *r*, that the path of *r* is practically a straight line.

The coupling link K therefore corrects the circular movement of the axis *l* to a linear movement of *r* proportional to the movement of the point of contact e_1 between the bell-crank and the pin *p*, which contact point moves in a straight line without sensible error.

The coupling link K serves also another purpose, namely to prevent the extension of the part of the apparatus above the upper gauge point *q*, *q*, and the upper support of the weigh-bar from being recorded on the plate. The extension of the part above *q*, *q*, has the effect of displacing the fulcrum H vertically by an amount equal to the elastic extension of the weigh-bar and the extension of about 1 inch of the specimen above the axis *qq*. This vertical displacement of H downwards merely turns the link K about the axis *r* and produces no sensible horizontal movement of *r*, and therefore the vertical displacement of H is not recorded on the plate.

The lever V is connected to an arm clamped on the mirror axis by the coupling rod U, so that the angular displacement of the arm V is communicated to the arm on the mirror axis without sensible error.

Contact at all points through the linkage is maintained by the weight *w*, which is carried by an arm clamped to the axis of the mirror, and it thus exerts a constant turning moment on the arm and maintains a constant pressure at all points of the linkage down to the final point of contact between the arm of the bell-crank lever and the lower axis, *pp*, at e_1.

The linkage thus converts the vertical extension of the specimen between the gauge points *p*, *p*, and *q*, *q*, into a proportional horizontal displacement of the point *r* without sensible error, and the consequent angular displacement of the hanging lever is communicated to the arm on the axis of the mirror M, suitably changed in magnitude so that the full range of the spot of light on the plate corresponds to the full extension of the specimen between the gauge points.

When the specimen breaks, the bottom frame *f*, with the screws *p*, *p*, still gripping the specimen, drops away with the lower part of the specimen. A stop limits the motion of the arm carrying the weight *w*.

There is geometric contact at all the link joints. When the apparatus is set up and the spot of light is brought to some convenient zero on the ground-glass focussing plate of the camera, the linkage may be displaced in any way and the spot always comes back to the zero with a snap as the point of contact e_1 is made.

This linkage has the valuable property that the movement of the spot of light can be accurately calibrated *in situ*. This is done by means of a calibrating step gauge like a ladder with steel rungs set accurately at half an inch apart. When the apparatus is set up and an experiment is about to begin the spot of light is brought to a convenient zero. The step gauge is placed on one of the lower pins *p*, *p*, and the frame G and with it the bell-crank lever is drawn slightly away from the specimen and then replaced, but with the end of the bell-crank lever resting not on the pin *p* but on a pin in the step gauge half an inch below it. The corresponding movement of the spot of light may then be observed directly on the focussing plate, or if a photo record is to be taken a slight movement of the jockey weight on the beam produces a slight displacement of the spot at right angles to the extension axis of the record, and thus when the plate is developed an index mark appears at a distance from the origin corresponding to a half-inch movement of the point of contact e_1 in a vertical direction. The plate may be calibrated in this way at half-inch intervals, or even quarter-inch intervals, if desired. In practice, however, it is only necessary to obtain one or at most two such marks, because the movement of the spot is proportional to the extension of the specimen without sensible error, and a full scale

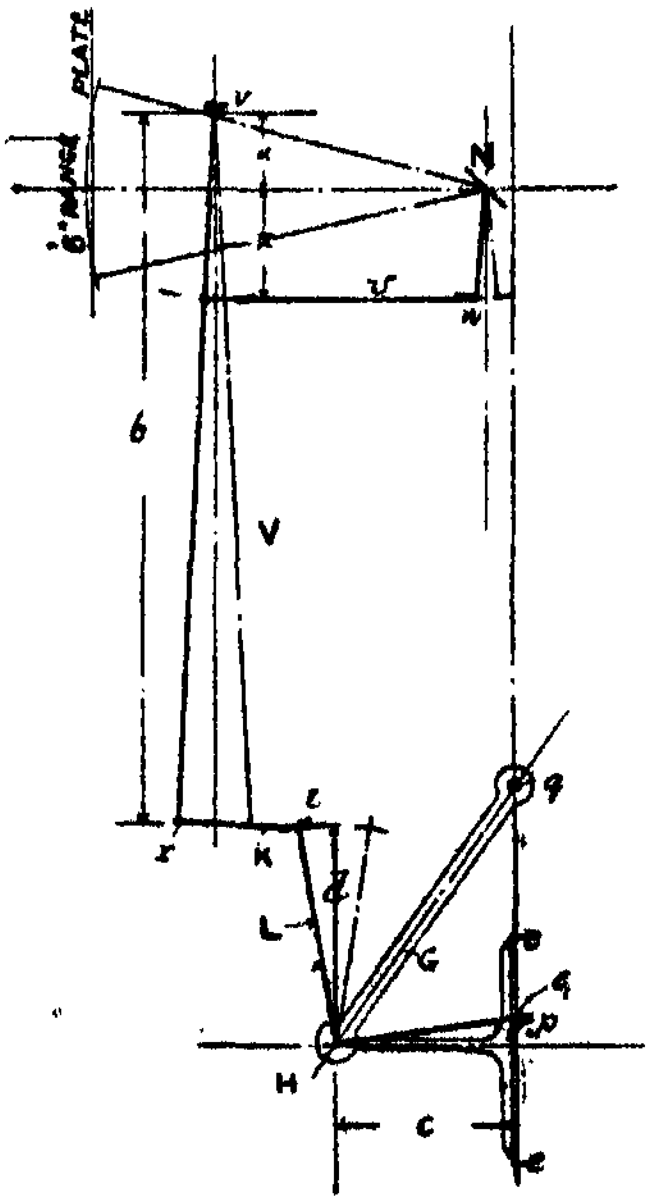

FIG. 4.—Centre line sketch of extension linkage.

can be constructed from the marks obtained *in situ* after the diagram is developed.

Another convenient property of the linkage is the ease with which the scale of the diagram may be changed. This will appear from a consideration of the dimensions of the linkage. Referring to the centre line diagram of the linkage in fig. 4 it will be observed that the maximum range of the spot of light is 6 inches. The focussing plane is about 12 inches from the mirror N, hence a range of 6 inches corresponds with an angular movement of the mirror of a quarter of a radian. Let x be the length Nn of the arm fixed to the mirror shaft, and let h be the horizontal displacement of its end, then the spot has passed over its full range when

$$h/x = \tfrac{1}{4}. \qquad (1)$$

Let l be the extension of the specimen between the gauge points; c and d the lengths of the arm of the bell-crank lever; b the length of the hanging lever V, and $(a+x)$ the distance from the axis of V to the point at which the coupling rod is attached. Then

$$h = \frac{d(a+x)l}{bc}, \qquad (2)$$

which by the aid of (1) gives

$$x = \frac{d}{c}la \bigg/ \left(\frac{b}{4} - \frac{d}{c}l\right), \qquad (3)$$

from which the magnitude of x can be calculated in order that an extension l between the gauge points may produce a movement of the spot of light over the whole range of 6 inches.

In the actual instrument

$$a = 3 \text{ inches}, \quad b = 22{\cdot}9 \text{ inches}, \quad c = 4 \text{ inches}, \quad d = 5{\cdot}625 \text{ inches},$$

so that

$$x = \frac{4{\cdot}218\,l}{5{\cdot}725 - 1{\cdot}406l}. \qquad (4)$$

Let the total extension to be provided for be 2 inches. Then, inserting 2 for l in (4), $x = 2{\cdot}9$ inches, that is to say, an extension of 2 inches will produce a movement of the spot over the full range of 6 inches.

The arm and the hanging lever V, coupled by the rod U, are slotted, so that an adjustment of x can be readily made without disturbing any other part of the apparatus.

An exact adjustment of x is not necessary, because every diagram is calibrated for extension when the specimen is *in situ*, and just before the load is applied to the specimen, in the way explained above.

Method of Making a Test.—When the specimen is in place and the apparatus set up, the first step is to bring the spot of light to the point on the focussing plate which is to be the origin of the diagram. This can be easily and quickly done by means of the adjustment provided. Then, after the plate has been inserted in place, the beam is balanced at a moderate load, usually about half a ton. The step gauge is then inserted between the end of the bell crank lever and the lower points, *p*, *p*, and two or three lines drawn on the plate at known distances from the origin in the way explained above. The beam is next carefully balanced at 1 ton, and, when it is standing midway between the stops, and quite free from vibration, the hanging lever V is drawn back and replaced, in order that the spot of light may move over the plate in a direction parallel to the extension axis, and thus fix a line in the load scale corresponding to 1 ton. The load scale, photographed on a separate plate, is afterwards applied to the photographic record, so that the lines marked 1 ton on each coincide, in order to read off the load corresponding to any point on the diagram.

After drawing the 1-ton line the lever is dropped to the lower stop, and the jockey weight is run out to 12 tons. The load is then applied to the specimen by starting the hydraulic ram connected with the straining cylinder, which is kept going until the specimen breaks.

If the specimen requires more than 12 tons to break it, the beam lifts, and thus prevents the weigh-bar from being overstrained. In fact, the beam and the jockey weight may be regarded as a safety device, to show when the load applied by the straining cylinder exceeds the maximum load for which the weigh-bar is designed.

The load scale of the apparatus is shown by photo. fig. 5. It is obtained by connecting the weigh-bar to the bottom shackle of the machine, and then balancing the beam at a series of loads and at each load giving the mirror axis N a small angular displacement by hand. The instrument is shown in position in the testing machine, with a specimen attached to the weigh-bar, and with the extension apparatus in place, in fig. 6.

Diagrams Obtained with the Instrument.—A typical diagram for a piece of mild steel is shown in fig. 7. The load at any point is obtained by placing the load scale of fig. 5 over the diagram so that the 1-ton lines coincide. The extension scale is fixed by the ½-inch calibration marks obtained by the step gauge.

It will be seen from the diagram that the load rises to a maximum value of 6¼ tons and then drops back to about 5·4 tons. The metal then draws out with small variations of load until at an extension of 0·12 inch the curve becomes smooth and rises to the maximum load of 8 tons. After this the curve drops smoothly to the point at which fracture takes place. This point is well defined in the diagram, because at the instant of fracture

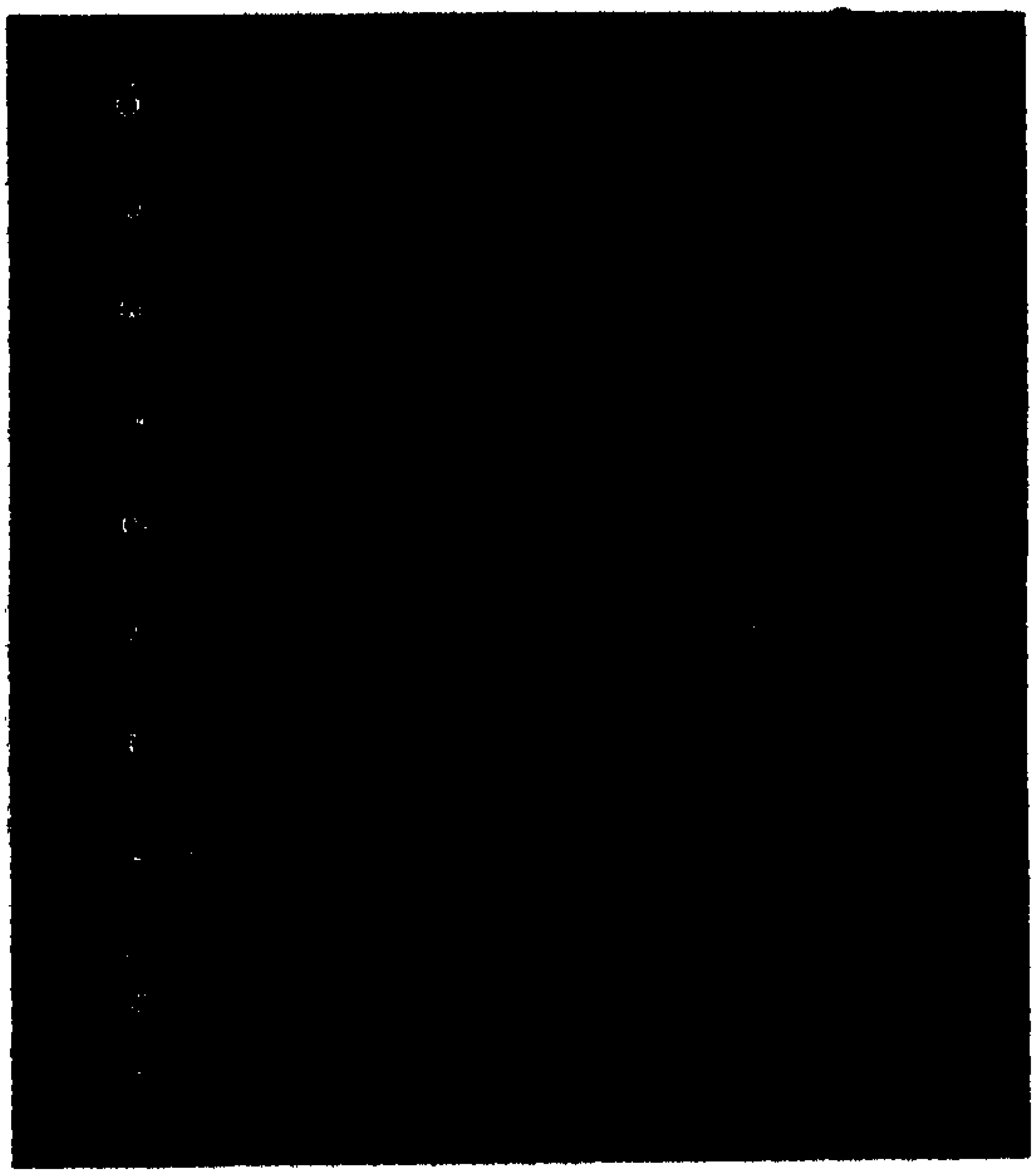

Fig. 5.—Photograph of load calibration.

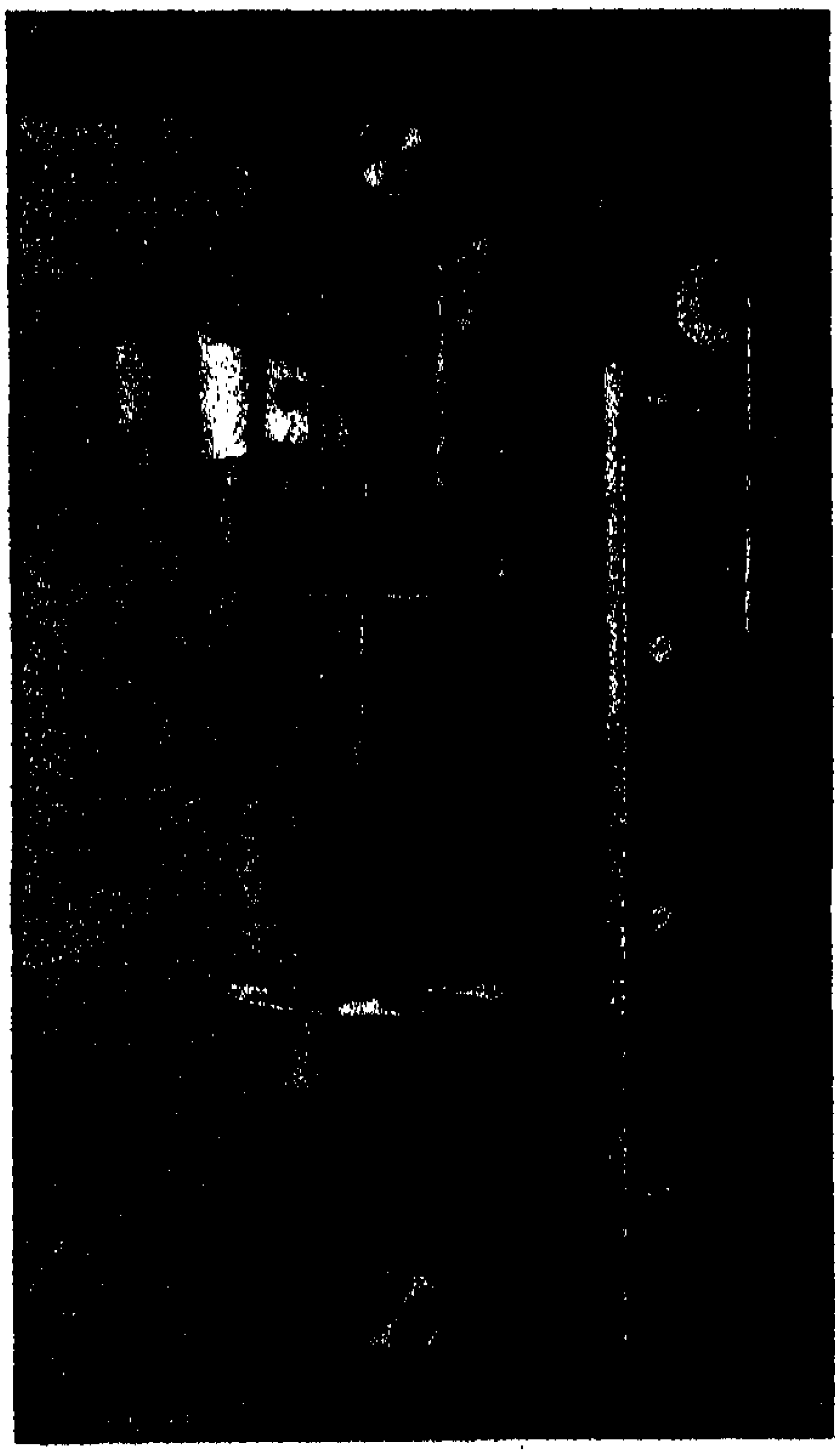

Fig. 6.—General view of indicator in the testing machine.

Fig. 7.—Load-extension diagram of mild steel.

the spot of light starts to move so rapidly that no impression is made on the plate.

The time occupied in breaking the specimen was three minutes, approximately.

The extension of the specimen measured 1·64 inches on a gauge length of 5 inches, with a reduction of area at the fracture of 64 per cent.

The total extension scaled from the diagram is also 1·64 inches.

In order to get some idea of the time occupied by the successive characteristic phases of the break, a mild steel specimen turned from the bar from which the specimen whose load-extension diagram shown in fig. 7 was cut was broken by steadily working the ram and thus steadily increasing the strain, and the spot of light was followed on the ground glass focussing plate with a pencil, and the times at which the spot arrived at different points on the curve were recorded by means of a chronograph, the key of which was placed close to the machine so that it could be operated with one hand whilst the point could be marked on a plate with a pencil in the right hand.

The total time of the break was increased to about six minutes in order to get a better idea of the relative time occupied in the parts of the curve where the movement of the spot is most rapid.

The general characteristics of the diagram as regards time are as follows:— The spot moved steadily from *a* to the point of maximum load *b* (fig. 8) in 50 seconds, and then dropped to the point *c* in a time estimated at a quarter of a second, and then moved along the irregular path from *c* to *d* in about

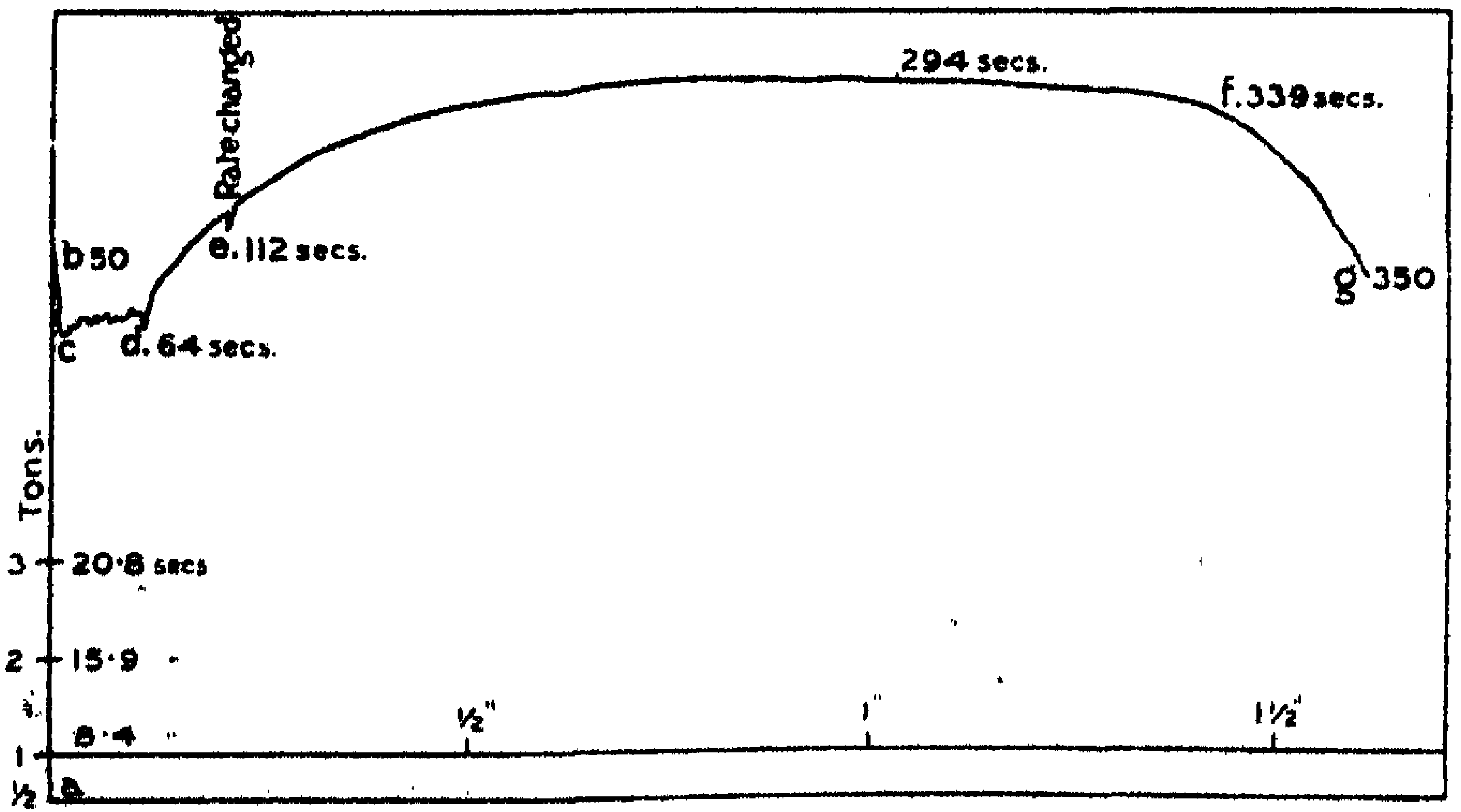

Fig. 8.—Giving times at which spot passed various points in a load-extension diagram of mild steel.

fourteen seconds. When the spot arrived at the point *e* the rate at which the specimen was extended was increased to the same rate as that used in connection with the load-extension curve shown in fig. 7. The time at which the spot passes the point of maximum load is shown against the curve in the diagram. To an observer the spot appears to move with uniform speed along the curve from *e* to *f*, and then to quicken gradually towards the point of fracture *g*.

The sudden drop from the maximum elastic load carried by the specimen to an indefinite relation between the load and the extension and the subsequent definite relation during the plastic yielding characterises all the diagrams which were taken of mild steel and iron, as will be seen in the diagrams shown in fig. 10. With copper, however, there is no complicated relation at the yield point. The passage from the elastic state to the plastic state is pretty sharply defined, as will be seen from fig. 9, which is the load-extension diagram of a piece of copper containing 0·295 per cent. of arsenic.

FIG. 9.—Load-extension diagram of copper.

Load-extension diagrams of a series of three steels containing increasing percentages of carbon have been taken, and also a diagram from a piece of Farnley iron. All the diagrams are shown in fig. 10 reduced to a common load scale and to a common extension scale for purposes of comparison.

The extreme points of the curves shown in the photographs are well defined, and therefore the actual loads on the respective sections at the instant of fracture can be measured off the diagrams with accuracy. The stress calculated from the actual load and the fractured area measured from the broken bar is calculated for each of the specimens shown in fig. 10 and it is plotted vertically above the extreme point of each diagram. The chain-dotted curve connecting these points with the respective regions of maximum stress is sketched in roughly to indicate the form of the load-extension diagram at the particular section at which fracture occurred.

Thus in the case of the uppermost curve the maximum load carried was 42 tons per square inch, and the load on the fractured area was 61 tons per square inch.

The three steels shown in fig. 10 have approximately the same percentage composition as regards silicon, sulphur, phosphorus, and manganese, but have different percentages of carbon. With the exception of copper the extensions were taken on a gauge length of 5 inches. The copper specimen was gauged on 4½ inches.

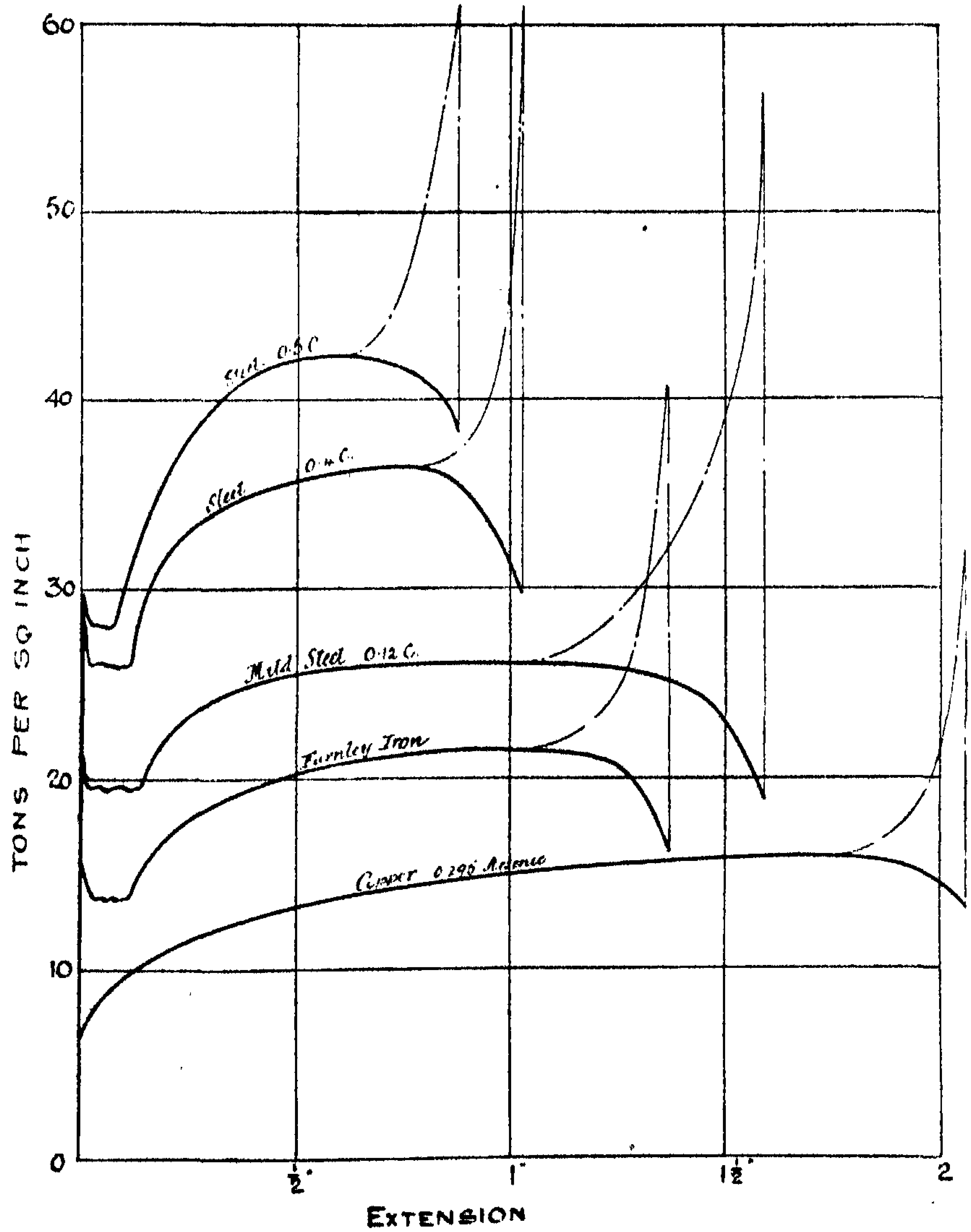

FIG. 10.—Load-extension diagrams reduced to common scales of load and extension.

These diagrams are shown in order to indicate the possibilities of the instrument. It is proposed to make a series of tests on the various kinds of metals used in the industries particularly with the object of investigating the region immediately beyond the elastic limit and the effect of suddenly applied loads and loads applied very gradually. The characteristic of the method of applying the load in all the diagrams shown is that the rate at which the extension of the specimen increases is approximately constant, because the pressure is applied to the straining cylinder of the testing machine by a ram driven in at a nearly constant rate. The rate at which the load is applied is therefore variable, as will be understood from fig. 8. The scale of the extension can in the particular instrument described be magnified conveniently about eight times, so that it is only suitable for investigations outside the true elastic region. The author hopes to communicate a paper shortly giving the description of a similar instrument for obtaining automatic diagrams within the elastic region.

The Passage of Homogeneous Röntgen Rays through Gases.

By E. A. Owen, B.Sc., 1851 Exhibition Scholar of the University College of North Wales, Trinity College, Cambridge.

(Communicated by Prof. Sir J. J. Thomson, F.R.S. Received February 8, and in revised form March 11,—Read March 21, 1912.)

Introduction.

The phenomena attending the passage of Röntgen rays through gases has been examined by several experimenters. The relative ionisation produced in different gases was investigated early in the history of Röntgen rays by Perrin* and Rutherford,† and later by Sir J. J. Thomson,‡ Strutt,§ McClung,‖ Eve,¶ Barkla,** and Crowther.†† Some of these experimenters allowed the rays to strike the electrodes and the walls of the ionisation chambers; this gave rise to corpuscular radiation which was totally absorbed in the gas, so that the ionisation observed was higher than the true value, and consequently the apparent relative ionisation was smaller than it should be for those gases in which the ionisation is greater than in air. Sir J. J. Thomson, McClung, and Crowther took precautions against this source of error, but in every case rays direct from a Röntgen bulb were used, and these rays were necessarily heterogeneous, and the heterogeneity was different in the various bulbs. In experiments on the relative ionisation in gases by Röntgen rays, not only rays of exactly the same hardness and the same intensity should be used to ionise each gas, but in order to obtain quite definite results it is necessary to use rays of quite a distinct hardness. Barkla's discovery of homogeneous rays emitted by different metals when Röntgen rays fall upon them makes it possible to use rays of a definite hardness. Such homogeneous rays have been used by Barkla to investigate the amount of ionisation relative to air produced in different gases and vapours.

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* Perrin, 'Ann. de Chimie et de Phys.,' 1897, vol. 11, p. 496.

† Rutherford, 'Phil. Mag.,' 1897, vol. 43, p. 241.

‡ J. J. Thomson, 'Camb. Phil. Soc. Proc.,' 1900, vol. 10, p. 10.

§ Strutt, 'Roy. Soc. Proc.,' 1903, vol. 72, p. 209.

‖ McClung, 'Phil. Mag.,' 1904, vol. 8, p. 357.

¶ Eve, 'Phil. Mag.,' 1904, vol. 8, p. 610.

** Barkla, 'Camb. Phil. Soc. Proc.,' 1909, vol. 15, p. 257; 'Phil. Mag.,' 1910, vol. 20, p. 370.

†† Crowther, 'Roy. Soc. Proc.,' 1908, vol. 82, p. 103.

The main object of the following research is to investigate more fully the various phenomena observed when homogeneous rays pass through gases composed of elements in the group in which no appreciable homogeneous radiation has been detected for rays of penetrating power within the range of that of those homogeneous beams emitted by metals of atomic weight from iron to silver. The gases used are air, carbon dioxide, and sulphur dioxide. The investigation may be divided into three parts—

(1) The absorption of homogeneous rays.

(2) The variation of ionisation with pressure.

(3) The ionisation, relative to air, produced in a gas by rays of different hardnesses.

Apparatus.

In the present work we deal with narrow pencils of homogeneous Röntgen rays. It was found very difficult to obtain a sufficiently intense pencil by placing a piece of metal in the path of the rays from an ordinary type of bulb; in this case only a small solid angle of rays emanating from the anticathode could be utilised to produce a secondary homogeneous beam, and in addition the rays had to traverse the glass wall of the tube and a certain column of air before they fell on the radiator, so that their intensity was greatly diminished. The problem therefore is to construct a bulb which will allow the primary rays to strike the radiator immediately after they leave the anticathode, and consequently reduce the size of the radiator, which would still envelop a greater solid angle of rays than would be the case in an ordinary bulb with a much larger radiator. The following is an account of an attempt made to construct such a bulb which could be used with the same ease as an ordinary type of bulb:—

The bulb is designed to have the anticathode on the surface. Since it is to be permanent and capable of being run for any reasonable length of time it is essential that no wax joints be used in its construction. A glass-metal air-tight joint had therefore to be used. The joint adopted was that used by Roebuck* in experiments on "The Bursting Strength of Glass Tubing." The principle of the method is as follows:—A thick glass tube, diameter about 2·5 cm., is taken and the outside carefully cleaned. A coating of platinum is spluttered over this tube for about 5 cm. of its length. This is done by brushing over the glass with a water solution of platinum chloride and dextrin containing 1 to 2 per cent. of each; the tube is then gently heated until the solution dries up, and afterwards it is incinerated in a Bunsen flame. After this process a thin conducting semi-transparent film of platinum is left on the glass. To secure a perfectly continuous layer all over the surface, two or three coatings of platinum are added in a similar way. It is essential to get a continuous layer of platinum on the glass tube, and to get it the glass surface must be very clean; distilled water should also be used to make up the solution of platinum chloride and dextrin. The next step is to deposit electrolytically a thick layer of copper on the platinum. The deposit should be very fine, so as to obtain a smooth surface on the copper. A very small current is therefore sent through the voltameter. A layer of copper, about 1 mm. thick, is deposited in this way. The glass tube is now ready to be soldered on to any metal tube which fits over it. Preliminary experiments on this method showed that the joint was quite air-tight, even when the metal tube was simply soldered round its edge to the copper layer on the glass.

A large distilling flask, about 20 cm. in diameter, is taken and a wide piece of thick glass tubing, about 8 cm. in length, fused to it diametrically opposite to its neck and in line with it. Over about 5 cm. of this tube is deposited a thick layer of copper by the above described process. A brass cap B (fig. 1*a*) is now put over the end of the tube, the brass tube T fitting over the copper deposit. The edge of the tube T is carefully soldered on to the deposit on the glass. The other part of the cap B is a thick circular brass disc having a circular hole, 1 cm. in diameter, bored at its centre, and which is soldered to the other end of the tube T. Over this hole is soldered a piece of silver foil, thick enough to stop all cathode particles travelling with a velocity corresponding to an equivalent spark gap of 4 to 5 cm. The collar W allows cold water to circulate round the tube, thus keeping the joint cool. This glass-metal joint proved very satisfactory; no trouble at all was experienced in obtaining it air-tight.

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* Roebuck, 'Phys. Review,' 1909, vol. 28, p. 264.

The cathode is slightly concave, so as to tend to bring the rays to a focus on the silver window. The beam of Röntgen rays emerging from the window can be made very intense, and a very large solid angle of the rays can be utilised to produce secondary beams.

A silver anticathode is used because a beam of Röntgen rays is required which is sufficiently hard to stimulate the homogeneous beams of metals of atomic weight lower than silver. It was also preferred to platinum because the latter occludes hydrogen very rapidly when heated, and would therefore be unsuitable for this purpose. Silver, however, occludes oxygen, but the amount it occludes is inappreciable at the temperature to which the anticathode is raised. Platinum was not actually tried; possibly, with good cooling arrangements, it may be used.

The bulb is fitted with a palladium softener and is permanently connected to a Töpler pump and charcoal tube. The equivalent spark gap can be kept quite constant by manipulating the palladium softener and charcoal tube, or, when liquid air is not available, the Töpler pump. The equivalent spark gap was kept at 4·5 cm. and the coil worked with a Cox mechanical interrupter, which is much more satisfactory than any form of mercury break tried, in that it gives a much steadier discharge.

The bulb was fixed up in a lead box. The radiators were placed over the silver anticathode, as shown in fig. 1, and were held always in the same position by a little aluminium frame, which was rigidly fixed to the lead box. The dimensions of the aperture S in the lead box were 1·5 cm. by 4·7 cm., and the centre of the radiator was about 7 cm. from it. A small lead collar, 0·5 cm. high, was placed 1 cm. from the centre of the window, to stop any rays direct from the bulb from passing through the aperture S. The beams sent out by the radiators were tested for their homogeneity before the rest of the apparatus was set up. This was done in the ordinary way, by putting an electroscope in the path of the rays and finding the percentage absorption produced by successive sheets of aluminium placed in front of it. The required homogeneity was detected.

A standardising ionisation chamber A, with central rod electrode, was placed in the direction of the rays at a distance of about 30 cm. from the aperture S. The inner surface of the chamber, together with the surface of the electrode, was covered with layers of filter paper, and the rays passed into the chamber through a parchment window. The electrode was carefully insulated from the chamber and was connected through an earthing key to a Wilson tilted electroscope, the needle of the earthing key being connected to a potential divider.

A second ionisation chamber B, which contained the gases under investigation, was placed parallel to the rays and at the same distance from the aperture S as the standardising chamber A. This chamber was 25 cm. long and contained two parallel aluminium electrodes at a distance of about 4½ cm. apart. One of these, *aa*, 24 cm. by 6 cm., was raised to a high potential, and the other, 18 cm. by 6 cm., connected through an earthing key to the potential divider and a second Wilson electroscope. The second of these electrodes was guarded at its ends by two plates of the same width and in the same plane as the electrode, and each 3 cm. long; the gap between the plates and the electrode was about 3 mm. wide. The plates were soldered to the ends of the chamber, which was earthed. The guard ring served to sweep away all the ions produced by the corpuscular radiation emitted from the ends of the chamber when the rays strike it, and the ions produced in the gas by the Röntgen rays, before coming to the region between the electrodes, *aa* and *bb*. The electrodes, guard plates, and the surface of the chamber were covered with layers of filter paper. The window through which the rays entered was of parchment, supported by two very thin crosspieces of aluminium. A lead screen was placed in front of the chamber, having a rectangular aperture in it measuring 1·8 cm. square. A pencil of

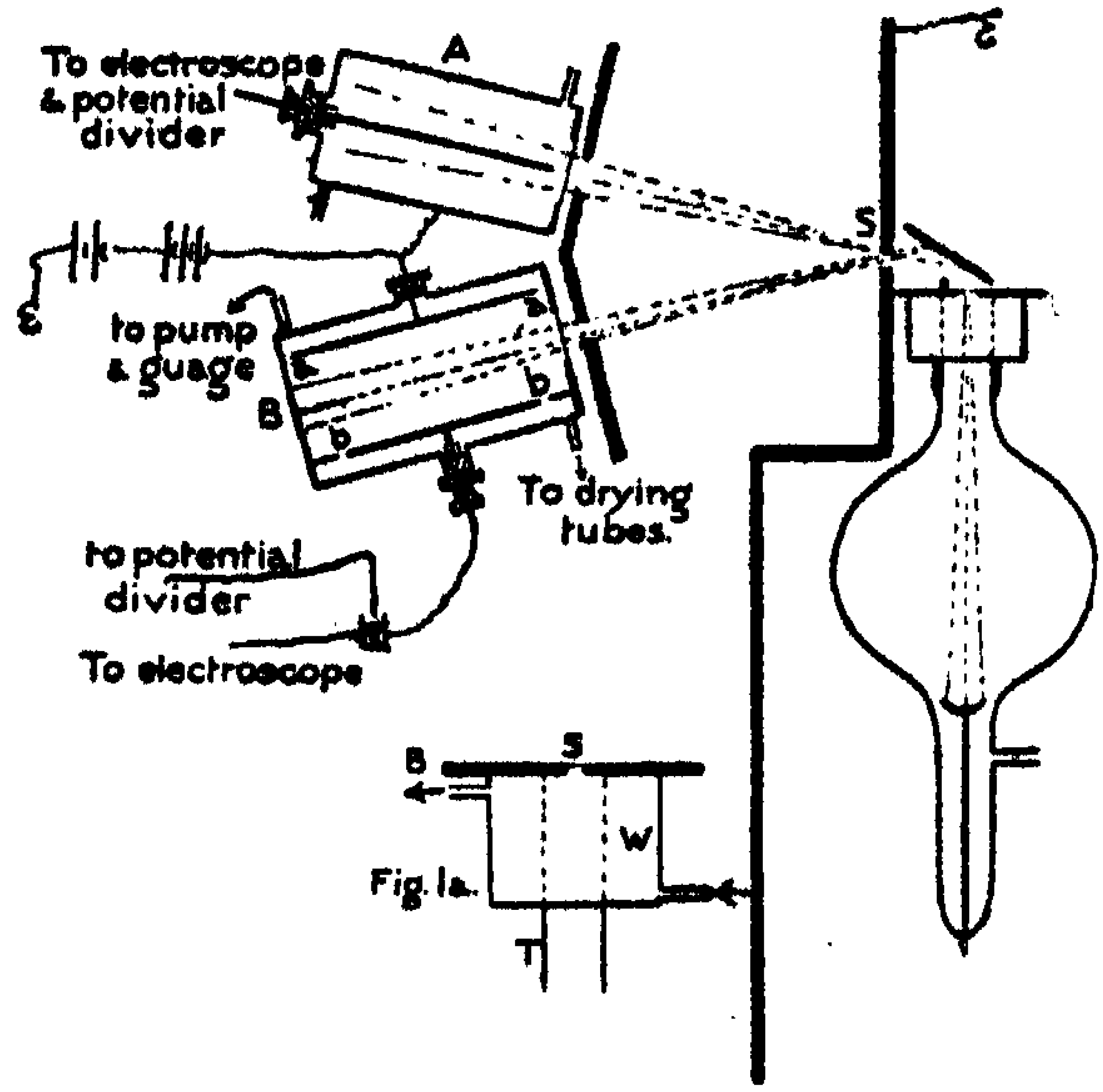

Fig. 1.

rays from the aperture S would then pass between the electrodes without touching them.

Both of the chambers were made air-tight; the chamber B was permanently connected to a Töpler pump and gauge. The same specimen of dried air was kept in the standardising chamber throughout the experiment; the other chamber was filled with the different gases examined, which were carefully dried and purified.

It was found that a potential of about 300 volts was ample to ensure saturation currents in the gases used. The electroscopes were worked at a sensitiveness of about 60 and 30 divisions per volt respectively. The readings could be taken very quickly. A certain fixed deflection was taken in the standardising electroscope in each case, and the corresponding deflection in the other electroscope observed. The rise of the potential of each leaf was immediately determined with the potential divider; in this case the error introduced is only that due to the fluctuation of the zero during the interval this potential was determined. This interval, however, was very short, and the leaves as a rule were very steady.

Absorption Experiments.

The first set of experiments were carried out to determine the absorption coefficient for different homogeneous beams in the three gases, air, carbon dioxide and sulphur dioxide. A wide brass cylinder, exactly 20 cm. long, with parchment windows at its ends, was placed directly in front of the chamber B and parallel to the rays coming from the radiators. It was made air-tight and connected to a gauge and a mercury pump. A lead screen with a small aperture in it was placed in front of the cylinder, so that only a narrow beam of rays passed through it.

In the case of air and carbon dioxide the absorption of the rays was measured at atmospheric pressure. The determination of the ionisation in B when the cylinder was evacuated, and afterwards when it was filled with the gas, sufficed to find the coefficient of absorption. The first reading gives a measure of the initial intensity I_0, and the second, the intensity I after passing through a column of gas 20 cm. long. Hence from the formula $I = I_0 e^{-20\lambda}$, λ, the coefficient of absorption in the gas (at that temperature and pressure) for the particular type of rays used is directly calculated.

With sulphur dioxide at atmospheric pressure it was found that the absorption was very great for the softest rays used—so great that the ionisation produced in the chamber B was almost inappreciable when bulb was run for about one minute. Readings were consequently taken with diminished pressures in the cylinder. Plotting the logarithm of the observed ionisation in the chamber B against the pressure of the gas in the absorbing chamber, we get straight lines for all the homogeneous beams used. These curves are shown in fig. 2.

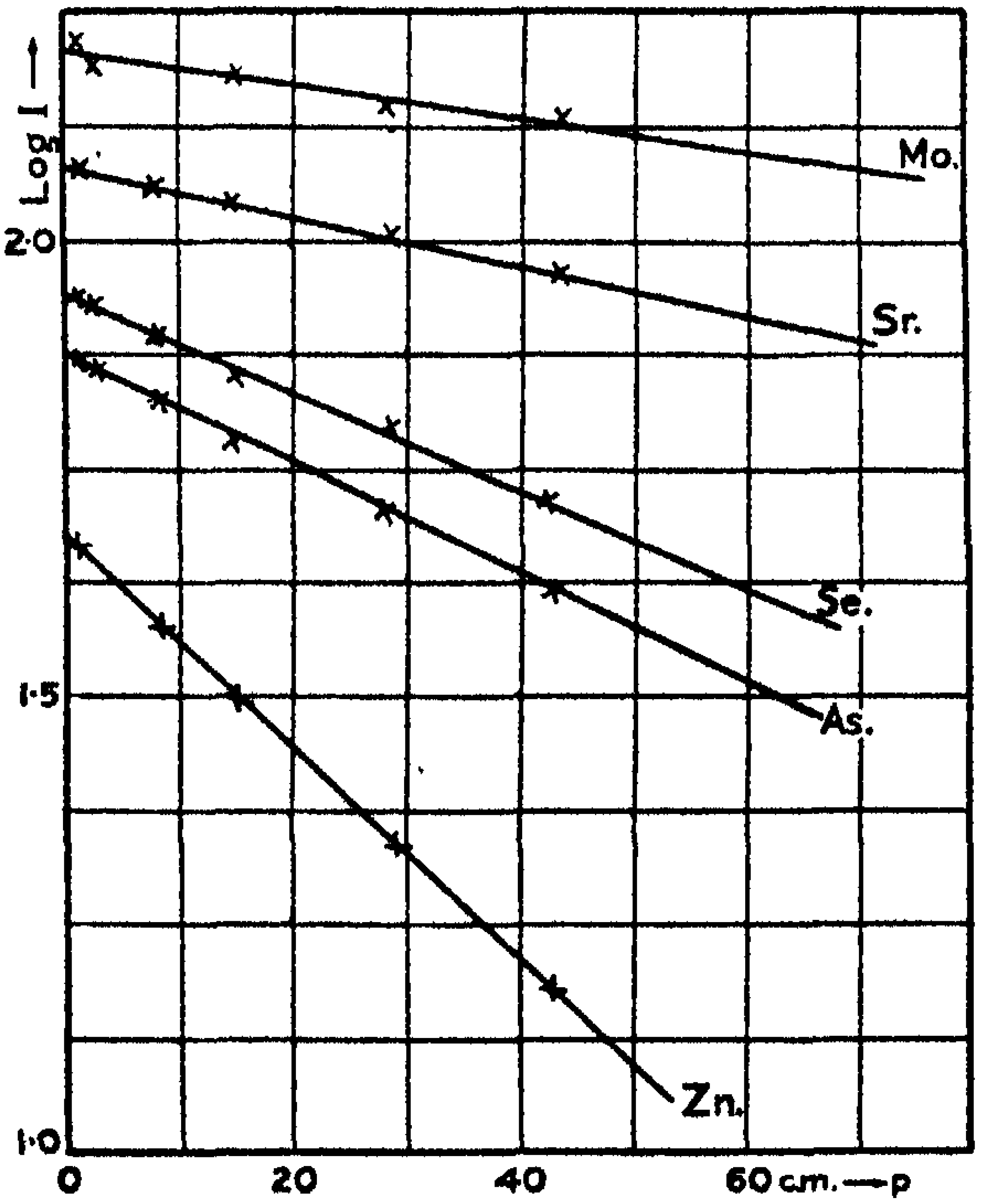

Fig. 2.

Hence the law of absorption for homogeneous beams in a gas becomes

$$I = I_0 e^{-\lambda p x/\pi},$$

when p is the pressure of the gas, and π the atmospheric pressure. From the curves in fig. 2 the absorption coefficient of the rays at atmospheric pressure can be obtained. The values of the coefficients of absorption, defined in this way, of the respective rays by the different gases at 0° C. and 760 mm. are given in Table I; the mass absorption coefficients are also tabulated for convenience.

Fig. 3 shows the relation existing between the atomic weights of the radiators giving out the homogeneous rays and the mass absorption coefficients of the different rays for any individual gas. The logarithm of the atomic weight of the radiator is plotted against the logarithm of the mass absorption coefficient. For each gas, the points lie on straight lines within the limits of experimental error, and these straight lines are parallel to each other. Hence the absorption coefficients of the different homogeneous

Table I.

Radiator.	Atomic weight of radiator. w.	Air.		CO$_2$.		SO$_2$.		λ/ρ.*		
		λ.	λ/ρ.	λ.	λ/ρ.	λ.	λ/ρ.	C.	Mg.	Al.
Fe	55·9	0·0254	19·72	0·0456	28·04	0·2673	91·2	10·1	80	88·5
Ni	58·7	0·0186	14·39	0·0319	16·10	0·1691	57·73	6·58	51·8	59·1
Cu	63·6	0·0130	10·08	0·0227	11·48	0·1404	47·90	5·22	41·4	47·7
Zn	65·7	0·0108	8·41	0·0184	9·29	0·1040	35·49	4·26	34·7	39·4
As	75·0	0·00592	4·59	0·00988	4·99	0·0548	18·60	2·49	19·3	22·5
Se	79·2	0·00442	3·43	0·00782	3·95	0·0449	15·31	2·04	15·7	18·9
Sr	87·6	0·00258	2·00	0·00420	2·12	0·0272	9·29	—	—	—
Mo	96·0	0·00166†	1·29	0·00281	1·42	0·0170	5·81	—	—	—

* Taken from Barkla and Sadler, 'Phil. Mag.,' May, 1909, p. 749.

† Deduced from the curve.

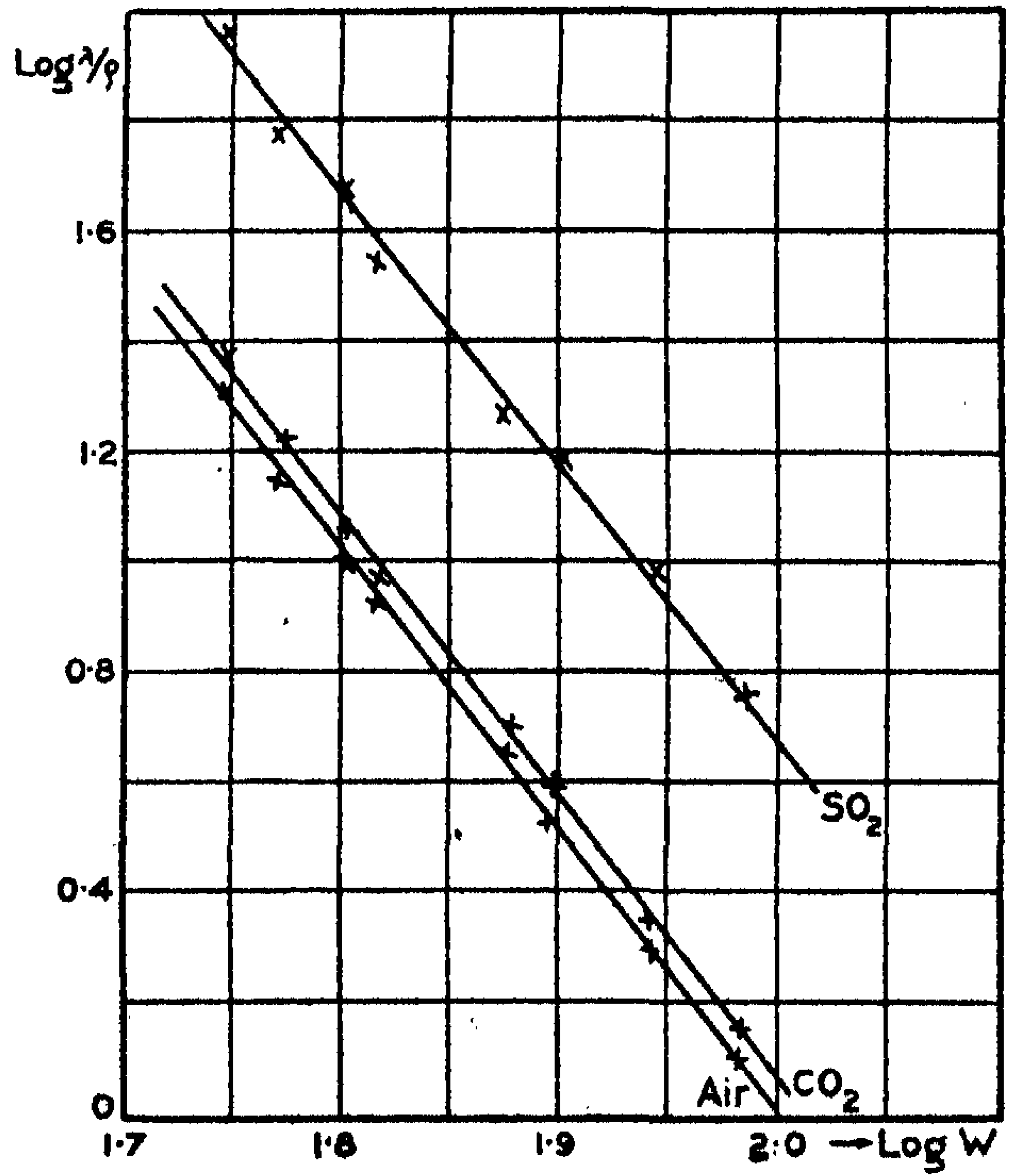

FIG. 3.

radiations in air are proportional to the absorption coefficients of those radiations in carbon dioxide or sulphur dioxide. Barkla and Sadler* found the same proportionality between the absorption coefficients of primary radiation by two elements, provided the primary radiation was not hard enough to excite the characteristic radiation of those elements.

* Barkla and Sadler, 'Phil. Mag,' 1909, p. 739.

Hence, generally, if ${}_X\lambda_A$ denote the coefficient of absorption of a certain radiation X in a substance A, whether elementary or compound (using the notation adopted by Barkla and Sadler),

$$\frac{{}_X\lambda_A}{{}_X\lambda_B} = \frac{{}_Y\lambda_A}{{}_Y\lambda_B} = \frac{{}_Z\lambda_A}{{}_Z\lambda_B},$$

provided the radiations X, Y, Z do not excite the characteristic radiations of the substances A and B. (When A and B are compounds the law does not hold if the rays excite the characteristic radiation of any one of the elements present.)

The straight lines in fig. 3 incline to the axis of abscissa along which $\log w$ is measured, at an angle $\tan^{-1}(-5)$ approximately, so that

$$\lambda/\rho = cw^{-5} \text{ (approximately)},$$

where c is a constant depending upon the nature of the absorbing medium.

Hence the coefficient of absorption of homogeneous Röntgen radiation in any of the gases investigated is approximately inversely proportional to the fifth power of the atomic weight of the element emitting the characteristic radiation. It is possible that the absorption of these rays follows the same law universally, whatever the absorbing medium may be. Taking, for example, the values given by Barkla and Sadler for λ/ρ in carbon, magnesium, and aluminium for the different rays, we find that the same law approximately holds also for these elements in the case of rays of penetrating power from iron to strontium radiation. It is desirable, however, that rays of a wider range of penetrating power be used before a general conclusion be arrived at, but, for the range of rays examined in the present work, the above relation undoubtedly approximately holds.

Ionisation and Pressure.

When a beam of Röntgen radiation passes through a gas it gives rise to both secondary Röntgen radiation and corpuscular radiation. With the pressures used in the experiment the corpuscular rays are totally absorbed, but this is not the case with the secondary Röntgen rays. The amount of secondary radiation produced in these light gases is, however, very small. Barkla finds that the energy of the secondary radiation proceeding from 1 cm. length of primary beam passing through air at atmospheric pressure and about 15° C. is 0·00024 of the energy of the primary radiation passing through. Consequently, the amount of ionisation produced by these secondary rays in the chamber is negligible compared with the whole amount of ionisation produced in the chamber. The only way by which these secondary rays can give rise to an appreciable amount of ionisation is by the production of corpuscular radiation if the rays were allowed to strike the metal electrodes and walls of the chamber. To avoid this, the electrodes and the walls of the chamber are covered with layers of filter paper. With this arrangement the amount of ionisation produced by the corpuscular radiation from the electrodes and the walls will be negligible, because the amount of corpuscular radiation sent out from the filter paper is of the same order as the corpuscular radiation produced in the gas, and, further, the corpuscular radiation sent out by the walls on account of the secondary rays penetrating the paper will be totally absorbed in the paper, and therefore not allowed to produce any ionisation in the gas.

In each gas there is a correction to be applied to the observed value of the ionisation due to the absorption of the rays in the gas before they reach the central plate electrode, and in the volume of gas under investigation between the electrodes. These corrections were rather small in air and carbon dioxide, but much larger in sulphur dioxide.

Some of the corrected results obtained with air and carbon dioxide are represented graphically in fig. 4. All the curves are straight lines through the origin.

In the case of SO_2 the method of procedure was somewhat different.

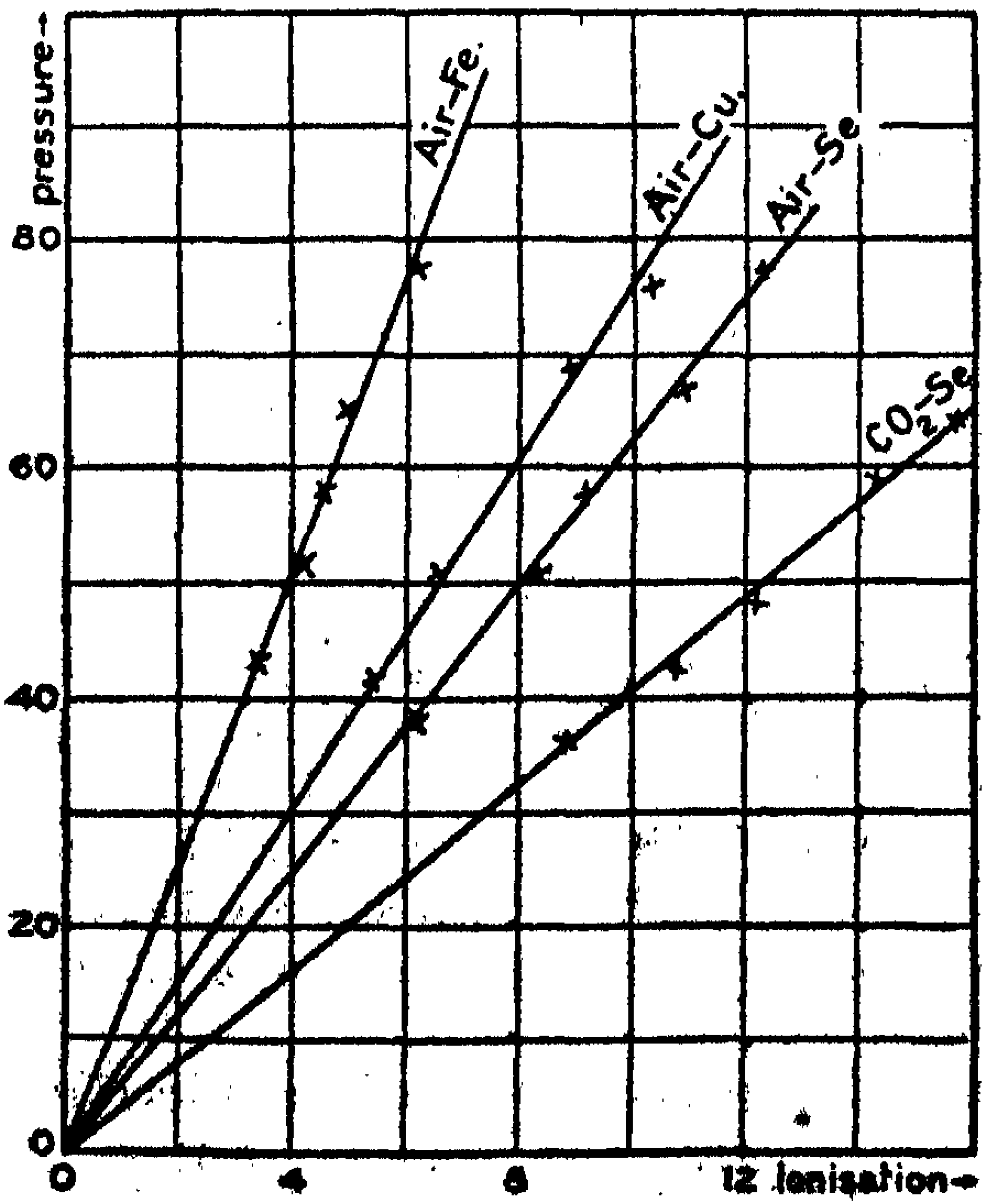

Fig. 4.

On the assumption that the ionisation is proportional to the pressure, it is very easy to calculate what the ionisation should be at any pressure, knowing the dimensions of the electrodes and guard ring and the coefficient of absorption of the rays in the gas.

Suppose a is the distance from the middle of the first gap to the parchment window, and b that of the second gap. Let I_0 be the intensity of the rays on the inner side of the parchment window, and let p be the pressure of the gas in the chamber. If λ is the coefficient of absorption of the rays in the gas at the given temperature and 760 mm. pressure,

The intensity of the radiation at a distance x from the end $= I_0 e^{-\lambda x p/\pi}$,

Ionisation produced at x in small layer dx $= \frac{p}{\pi} A I_0 e^{-\lambda x p/\pi} dx$,

where A is the ionisation produced by rays of unit intensity in travelling through a unit distance in the gas at atmospheric pressure.

$$\text{Ionisation produced between the plates} = \frac{p}{\pi} A I_0 \int_a^b e^{-\lambda x p/\pi} dx$$

$$= \frac{AI_0}{\lambda}\left(e^{-\lambda a p/\pi} - e^{-\lambda b p/\pi}\right);$$

i.e., say,
$$y = \frac{AI_0}{\lambda} z, \quad \text{where} \quad z = e^{-\lambda a p/\pi} - e^{-\lambda b p/\pi}. \tag{1}$$

The quantity AI_0/λ is a constant for the same gas for any particular type of rays used. All the quantities in the expression z are accurately determined. With the aid of these the value of z can be calculated for any pressure. These calculated values of z, multiplied by a constant, are in very close agreement with the observed values of the ionisation for all the pressures taken. Some of the curves obtained are shown in fig. 5. The agreement which exists between the calculated and observed values justifies the assumption that the ionisation in the gas is proportional to the pressure.

Relative Ionisation.

The ionisations in carbon dioxide and sulphur dioxide are calculated relative to air as a standard. The chamber B is initially filled with dry air and the ionisation produced in it by each of the homogeneous beams is measured. Dry carbon dioxide is then substituted for the air, and another series of observations taken with the gas at atmospheric pressure. In the case of sulphur dioxide, four sets of readings were taken with the gas at different pressures.

For any one definite type of rays we have by equation (1) for any gas

$$y = \frac{AI_0}{\lambda} z, \quad \text{and for air} \quad y_a = \frac{A_a I_0}{\lambda_a} z_a.$$

Hence A/A_a, the ionisation in the gas relative to air for that certain radiation, is equal to

$$y\lambda z_a / y_a \lambda_a z,$$

where y and y_a are the observed ionisations in the gas and air respectively,
λ and λ_a, the coefficients of absorptions of the rays in the gas and air respectively at the given temperature and 760 mm. pressure.
z and z_a are expressions defined by equation (1).

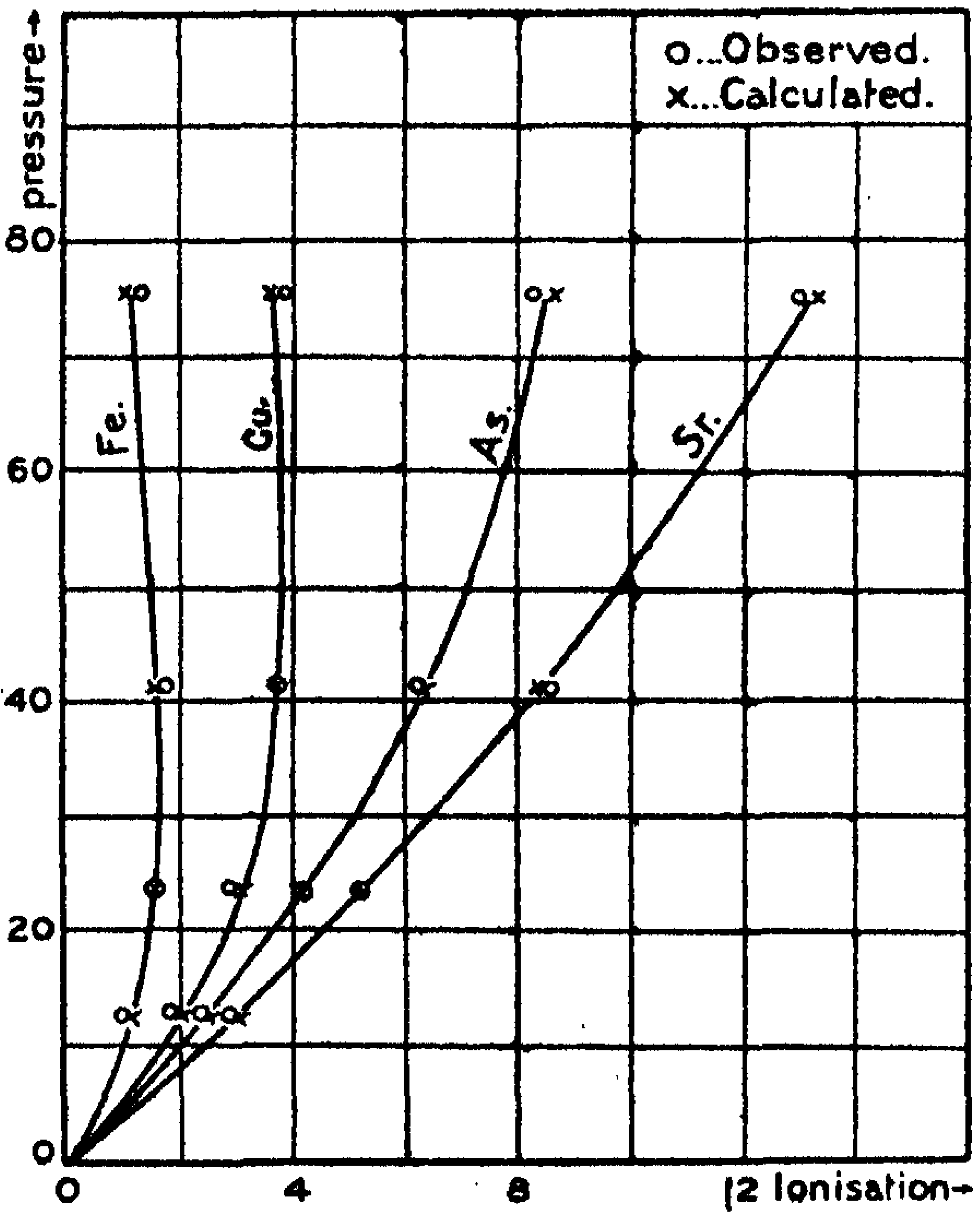

Fig. 5.

The calculated values of the relative ionisation for all the different rays are tabulated in Table II. Within the limits of experimental error, the relative ionisation is constant in the same gas for the range of rays employed.

Knowing the coefficient of absorption of all the rays in the different gases, we can find the relative total ionisation.

For the total ionisation produced in a gas at pressure p

$$= \frac{p}{\pi} A I_0 \int_0^\infty e^{-\lambda' x p/\pi} dx = \frac{A I_0}{\lambda'}.$$

where λ' is calculated from the values of λ given in Table I, allowing for scattering.

Hence T, the relative total ionisation $= A\lambda'_a / A_a \lambda'$.

Table II.

Radiator.	Relative ionisation in		Relative total ionisation in	
	CO_2.	SO_2.	CO_2.	SO_3.
Fe	1·581	11·34	0·90	1·07
Ni	1·546	11·57	0·88	1·25
Cu	1·552	11·84	0·89	1·08
Zn	1·538	11·52	0·91	1·18
As	1·510	11·73	0·91	1·22
Se	1·533	11·76	0·86	1·11
Sr	1·527	11·81	0·94	1·04
Mo	1·541	11·45	0·92	1·00

Table II gives the values of T calculated from this formula. It is observed that for the same gas the relative total ionisation is approximately constant for the range of rays used. There is a very great difference between the values of the relative ionisation in the two gases, but the difference between the relative total ionisation is comparatively small.

It appears, therefore, that for these light gases—the characteristic radiation of whose constituent elements has not been detected—the total number of ions produced by homogeneous beams of equal intensity is approximately the same in each gas for any particular type of rays.

Summary.

(1) The absorption of the different homogeneous radiations in a light gas, such as CO_2 or SO_2, is proportional to the absorption of those radiations in air.

(2) The absorption of homogeneous radiation in a gas is proportional to the pressure of that gas.

(3) For the homogeneous rays emitted by metals of atomic weight ranging from that of iron to that of molybdenum, the coefficient of absorption in the gases investigated is approximately inversely proportional to the fifth power of the atomic weight of the radiator which emits that characteristic radiation, *i.e.* $\lambda \propto w^{-5}$.

(4) The amount of ionisation produced in a thin layer of a gas is directly proportional to the pressure of the gas.

(5) The ionisation relative to air is approximately constant in the same gas for the different homogeneous rays.

(6) The total number of ions produced by homogeneous beams of equal

intensity is approximately the same in each gas for any particular type of rays.

In conclusion, I wish to acknowledge my indebtedness to Prof. Sir J. J. Thomson for his kindly interest and helpful suggestions throughout the course of the investigation.

Fluorescent Röntgen Radiation from Elements of High Atomic Weight.

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(Communicated by Prof. Sir J. J. Thomson, F.R.S. Received February 8,—Read March 21, 1912.)

A considerable amount of work has been done by various experimenters* showing that, when an element of higher atomic weight than calcium is subjected to a suitable primary beam of X-rays, the rays which leave the radiator consist of two types: firstly, the purely scattered radiation, which is almost exactly similar to the incident beam, and, secondly, a characteristic homogeneous radiation. The scattered radiation which in the case of a primary beam from an X-ray bulb is heterogeneous, is, with elements of low atomic weight, quite small in intensity when compared with the intensity of the homogeneous radiation which is emitted simultaneously. Owing to this fact, it is comparatively easy to prove that the elements with atomic weights between that of calcium and cerium give off when stimulated with X-rays homogeneous beams, and the hardness of the characteristic radiation from each of these elements has been measured by determining the absorption in aluminium. The radiations are usually defined by the value of their absorption coefficients, that is, by λ/ρ where $I = I_0e^{-\lambda x}$; ρ = density of aluminium. Using the values obtained, it is possible to plot a curve showing the relation between atomic weight and λ/ρ for the elements which emit a characteristic radiation, taking atomic weight as abscissa and λ/ρ for ordinates. If this is done, it will be found that the elements with atomic weights between that of calcium and cerium lie on an approximately smooth curve (Group K). When, however, the elements with higher atomic weight than silver are examined under suitable conditions, it is found that, with these elements, there are two distinct types of radiation: one, a hard characteristic radiation such as belongs to Group K, and superposed on this a very soft radiation. Prof. Barkla and Mr. Nicol* have investigated the soft radiations from the elements silver, antimony, iodine, and barium, and have shown that these elements, in addition to the usual characteristic radiation, emit another very soft radiation, which is also characteristic of the element. The values of the λ/ρ for these elements have been determined, and it has been shown, as far as it is possible with such soft rays, that they are homogeneous. If these values are plotted on the same diagram as that mentioned above, a second short curve is obtained, which can be continued to the X axis; when this is done, if this second curve resembles in shape the curve for Group K, it will pass before it reaches the X axis through the region of atomic weights between 184 and 238, which contains tungsten, gold, platinum, lead, bismuth, thorium, and uranium. This second series of elements has been designated Group L. Up to the present it has been impossible to draw this curve with any accuracy, as none of the elements between tungsten and uranium have been investigated as regards their X-ray properties.

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* Barkla and Sadler, 'Phil. Mag.,' Oct., 1908; Chapman, 'Phil. Mag.,' April, 1911; Barkla, 'Phil. Mag.,' Aug. 1910.

The following experiments were performed in order to see—

(1) Whether the radiations emitted by these elements when the scattered radiation was allowed for, were as homogeneous as those emitted by the elements of Group K.

(2) To investigate whether the same absorption phenomena are found with the elements of Group L as with Group K.

(3) To investigate whether there is an empirical relation between atomic weights of different elements emitting characteristic radiations of the same penetrating power as tested by the absorption coefficient.

The chief difficulty which has to be met, when examining the X-radiation from the elements in the second group (Group L), is the magnitude of the scattered radiation, this being heterogeneous, depending on the primary beam; it is, unless special precautions are taken, impossible to distinguish it from the supposed homogeneous radiation which it accompanies. With elements of atomic weight such as copper, the intensity of the scattered radiation is so small (sometimes less than 0·5 per cent. of the total radiation) that it can for all practical purposes be neglected, but, as the atomic weight rises, the intensity of the scattered radiation increases, for two reasons: firstly, for the same number of atoms present, there is a greater mass of scattering material; and, secondly, sufficient evidence has been obtained to show that the ordinary law of scattering of mass for mass the same, which has been shown to hold for all elements up to sulphur, ceases to be true when the heavier elements are considered. In a recent paper, Prof. Barkla* estimated that copper scatters about twice as much radiation as an equal mass of one of the lighter elements, such as sulphur, while it would appear that silver is six times as efficient a scatterer as sulphur, mass for mass. This difficulty, which begins to enter, even in Group K, with silver, will, with elements of atomic weight of the order of 200, enter to such an extent that if the radiation from an element of high atomic weight such as platinum was examined in the ordinary way, the great increase of scattered radiation would mask, if it did not completely swamp, any characteristic radiation which might be present. The method of attacking this difficulty was to so arrange the experiment that the intensity of the purely scattered radiation could be measured and subtracted. A description of the apparatus will serve to show the manner in which the correction for the scattered radiation was made.

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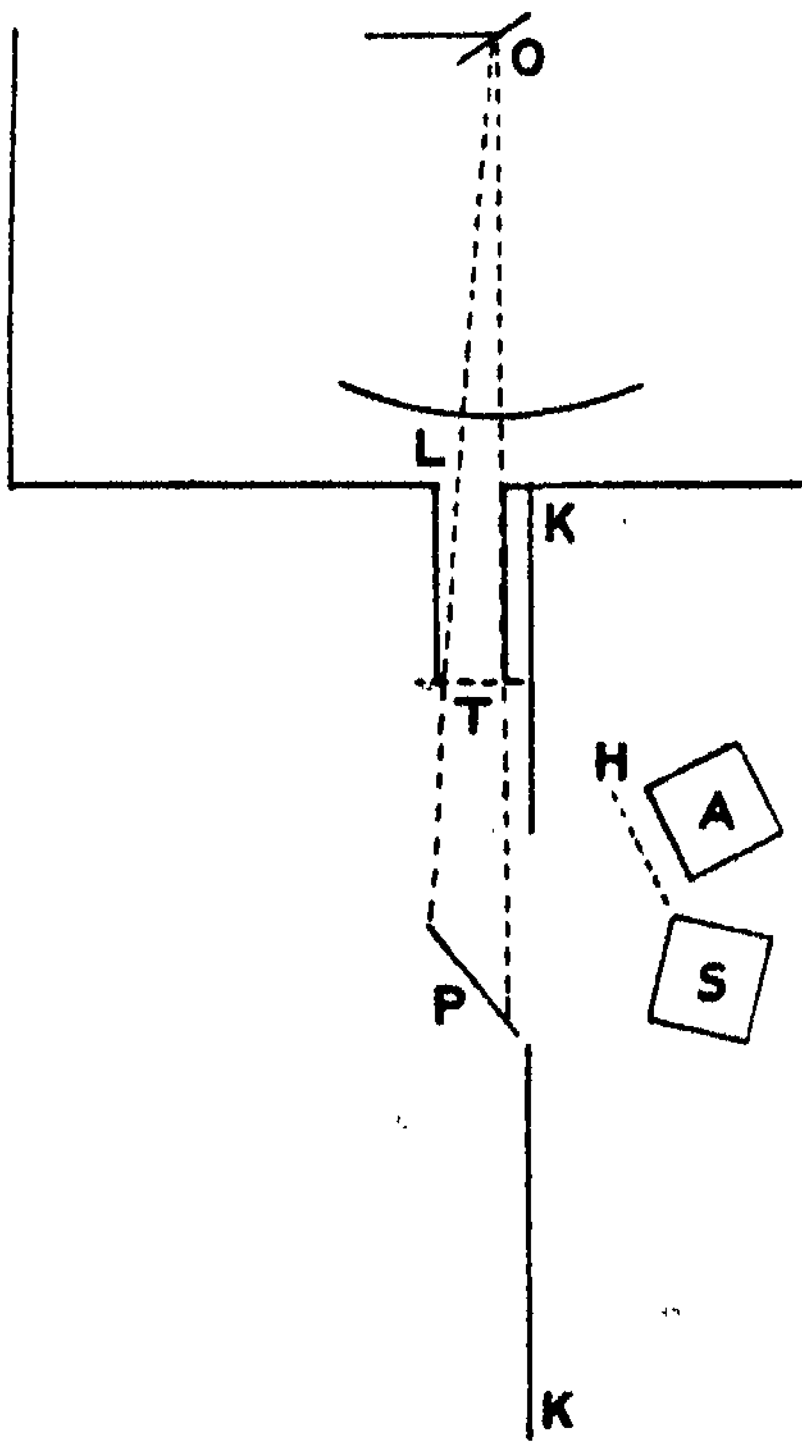
* 'Lond. Phys. Soc. Proc.,' Dec., 1911, vol. 24, part 1.



X-rays from the anticathode O passed through the slit L in the lead box on to the radiator in the position P. The radiation leaving the plate P passed through another adjustable slit in the lead screen KK, into the two electroscopes A and S. In front of the electroscope A was placed a stand in which the absorbing sheets were placed when the radiation was tested. The electroscope S simply served to standardise the intensity of the secondary radiation from the plate P. In order to limit the primary beam so that it fell almost wholly on the radiator P, the rays from the bulb were made to pass through a narrow lead tunnel, and at the end of this tunnel at T sheets of thick aluminium were placed so as to cut off all but the very hard radiation which is present in the beam. A factor which enabled the scattered radiation to be minimised, and which has perhaps not received the importance it should, is the advantage derived from using thin radiators. For, generally speaking, the homogeneous radiation, owing to its low penetrating power, comes only from a small depth. Any greater thickness than this depth does not serve to increase the intensity of the homogeneous radiation but merely increases the scattered radiation which is able to come from deeper layers. In these experiments very thin radiators were used but they were in all cases of sufficient thickness as to be considered of infinite depth from the point of view of the homogeneous radiation.

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* Barkla, 'Phil. Mag.,' Sept., 1911.

The ordinary method of determining the successive absorptions was used. The deflection in the electroscope A was first determined while the standardising electroscope underwent a certain deflection; a sheet was then placed in the stand H so as to absorb a portion of the rays passing into A, and the leak in A while the standardising electroscope suffered the same deflection was measured. From these values the percentage absorption of the radiation by each sheet was measured.

The method of subtracting the merely scattered radiation was as follows:—The bulb was worked until it was exceedingly hard with an equivalent spark gap of 5 or 6 inches. In addition to this the primary beam was made to pass through a thick sheet of aluminium (0·2 cm.) placed in the path of the beam at T; in this way all but the hardest constituent of the beam was stopped by the aluminium, thus a beam of X-rays of very great hardness was obtained. This penetrating primary when it fell on the radiator at P made it emit a radiation which consisted of (1) the supposed homogeneous constituent, (2) the superposed scattered radiation. This heterogeneous beam was then examined in the usual way; the effect of placing the sheets of aluminium in front of the electroscope A was to cut down the supposed homogeneous radiation, which was, of course, soft when compared with the scattered radiation for the elements experimented on in Group I. On the other hand, owing to its great penetrating power, the scattered radiation was not cut down to any great extent; in the case of gold, aluminium of thickness sufficient to cut off 99·9 per cent. of the homogeneous radiation, did not cut down the scattered radiation more than 10 per cent. When these successive absorptions had been taken, a thickness of aluminium (0·13 cm.) was placed in the stand H; this cut off, for all practical purposes, the whole of the homogeneous radiation. At the same time almost the whole of the hard scattered radiation still reached the electroscope. With this arrangement the amount of the superposed scattered radiation was measured by allowing the standardising electroscope to suffer the same deflection as in the previous absorption experiments, and noticing the deflection which the leak, due to the scattered radiation, produces in the electroscope A. From these values the total intensity of the scattered radiation can be readily found. If this constant factor is subtracted from the previous values, results are left which give not the absorption of the whole beam consisting both of scattered and homogeneous rays, but now only the absorption of the supposed homogeneous radiation. A typical account of this scattering correction is given in detail for the platinum radiation, for the other elements a correction of the same order has been made and the final results are stated.

Correction for the Scattered Radiation from Platinum.

The first column in the table below shows the number of sheets in front of the electroscope A, the second column the intensity of the total radiation (*i.e.*, scattered and homogeneous) after each successive absorption. The third column represents the intensity of the total radiation *minus* the scattered radiation, obtained by subtracting the scattered radiation as shown below:—

No. of absorbing sheets, each 0·0067 cm.	Intensity of total radiation (scattered + homogeneous).	Intensity of homogeneous radiation (total − scattered radiation).
0	54·6	50·1
1	38·3	33·8
2	27·5	23·0
3	20·1	15·6
4	15·2	10·7
5	11·7	7·2

Intensity of the scattered radiation as measured by passing the beam from the platinum radiator through 0·13 cm. of aluminium, which absorbs 99·9 per cent. of the homogeneous radiation and only 9·8 per cent. of the scattered radiation = 4·1.

Adding to 4·1 the 10 per cent. of the scattered radiation which is absorbed in the aluminium,

Total intensity of scattered radiation = 4·5.

Subtracting this as a constant factor from the values in Column 2, Column 3 is obtained.

If, now, $\log(I_0/I)$ for the total radiation from Column 2 and $\log(I_0/I)$ for (total radiation—scattered radiation) from Column 3 be plotted against thickness of aluminium absorbing, fig. 1 is obtained. It will be seen that the curve which represents the absorption of the total radiation becomes a straight line when the scattered rays are allowed for. That is, when the superposed scattered radiation is subtracted, there is left a homogeneous beam.

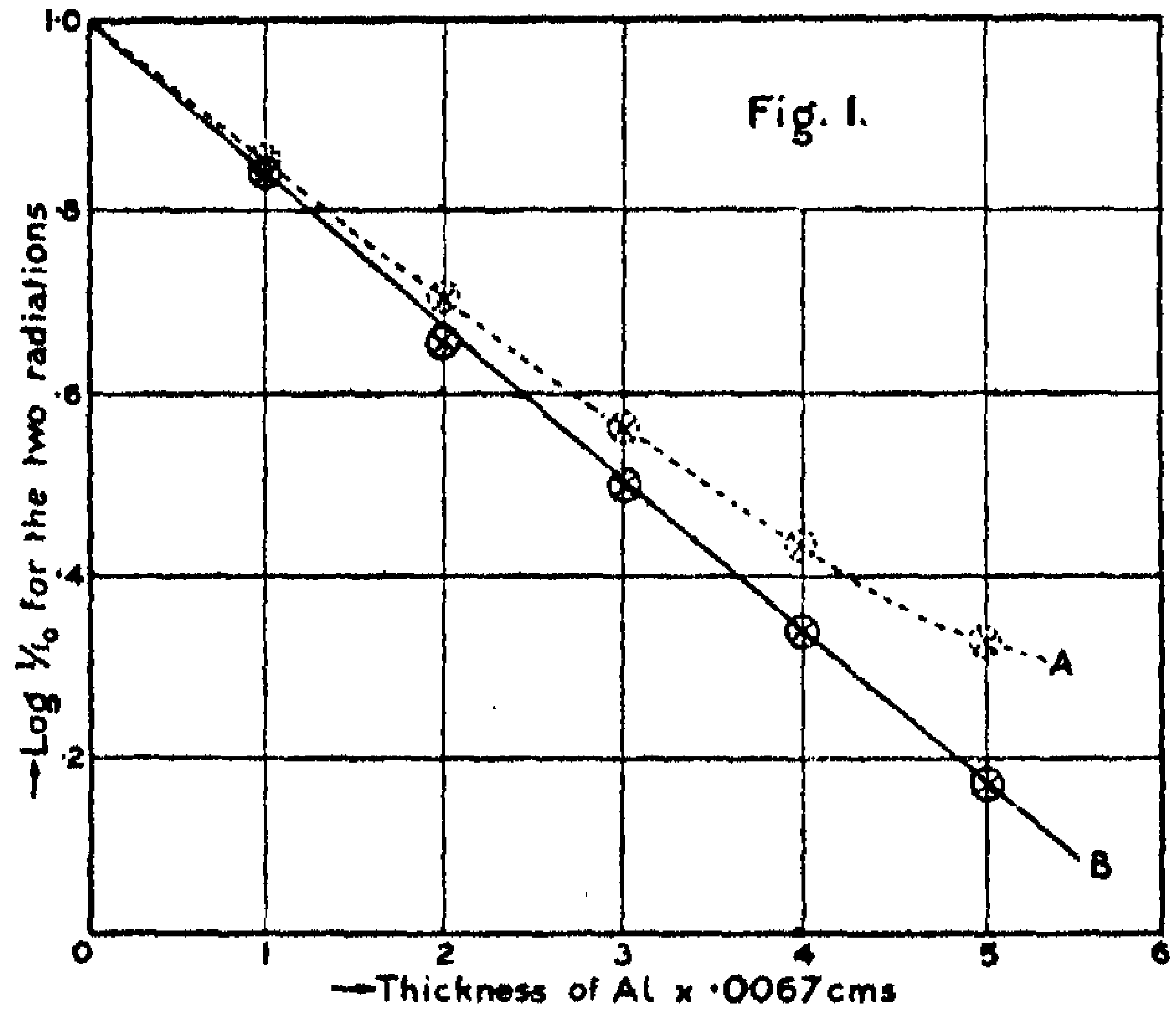
Fig. I.

Results showing the Homogeneity of the Radiations.

To measure the homogeneity of the rays from the various elements they were passed through plates of aluminium of different thicknesses and the percentage absorption of the emergent rays measured by a sheet of aluminium. In the tables below, the first column gives the percentage absorption of the rays by the different plates of aluminium; the second, the value of the percentage absorption of the emergent rays by aluminium (0·0067 cm.).

Tungsten.

Radiator .... Powdered tungsten metal.

Percentage absorption of rays by different plates of Al.	Percentage absorption of the emergent rays by Al (0·0067 cm.).
16	43·8
50	41·9
70	39·9
82	38·0
89	39·9
Mean value...............	40·7

$\lambda/\rho = 30{\cdot}0$.

Platinum.

Radiator .... Pure platinum foil.

Percentage absorption of rays by different plates of Al.	Percentage absorption of the emergent rays by Al (0·0067 cm.).
15	32·5
42	31·9
61	32·2
73	32·2
82	32·7
Mean value...............	32·3

$\lambda/\rho = 22{\cdot}2$.

Gold.

Radiator .... Pure gold plate.

Percentage absorption of rays by different plates of Al.	Percentage absorption of the emergent rays by Al (0·0067 cm.).
12	31·3
40	33·2
59	31·5
72	29·9
81	31·6
Mean value...............	31·5

$\lambda/\rho = 21{\cdot}6$.

Lead.

Radiator .... Pure lead foil.

Percentage absorption of rays by different plates of Al.	Percentage absorption of the emergent rays by Al (0·0067 cm.).
12	25·6
35	26·3
52	25·8
65	25·8
74	27·8
81	26·0
86	26·0
Mean value...............	26·2

$\lambda/\rho = 17{\cdot}4$.

Bismuth.

Radiator .... Powdered bismuth metal.

Percentage absorption of rays by different plates of Al.	Percentage absorption of the emergent rays by Al (0·0067 cm.).
10	23·7
32	24·2
49	24·5
62	24·5
72	24·3
79	25·0
Mean value...............	24·4

$\lambda/\rho = 16{\cdot}1$.

Thorium.

Radiator .... Powdered thorium oxide.

Percentage absorption of rays by different plates of Al.	Percentage absorption of the emergent rays by Al (0·0134 cm.).
5	24·6
29	25·7
46	24·4
59	25·1
69	25·5

Mean value............... 24·3

$\lambda/\rho = 8{\cdot}0$.

Uranium.

Radiator .... Powdered uranium oxide.

Percentage absorption of rays by different plates of Al.	Percentage absorption of the emergent rays by Al (0·0134 cm.).
4	24·9
26	22·6
43	23·2
56	23·3
66	23·1
74	23·1

Mean value............... 23·1

$\lambda/\rho = 7{\cdot}5$.

The relation between the thickness of aluminium absorbing and $\log(I/I_0)$ at each successive absorption is plotted in fig. 2 for the whole series of radiations, from the tables just given. The straight lines obtained indicate the almost exact homogeneity when the scattered radiation is subtracted.

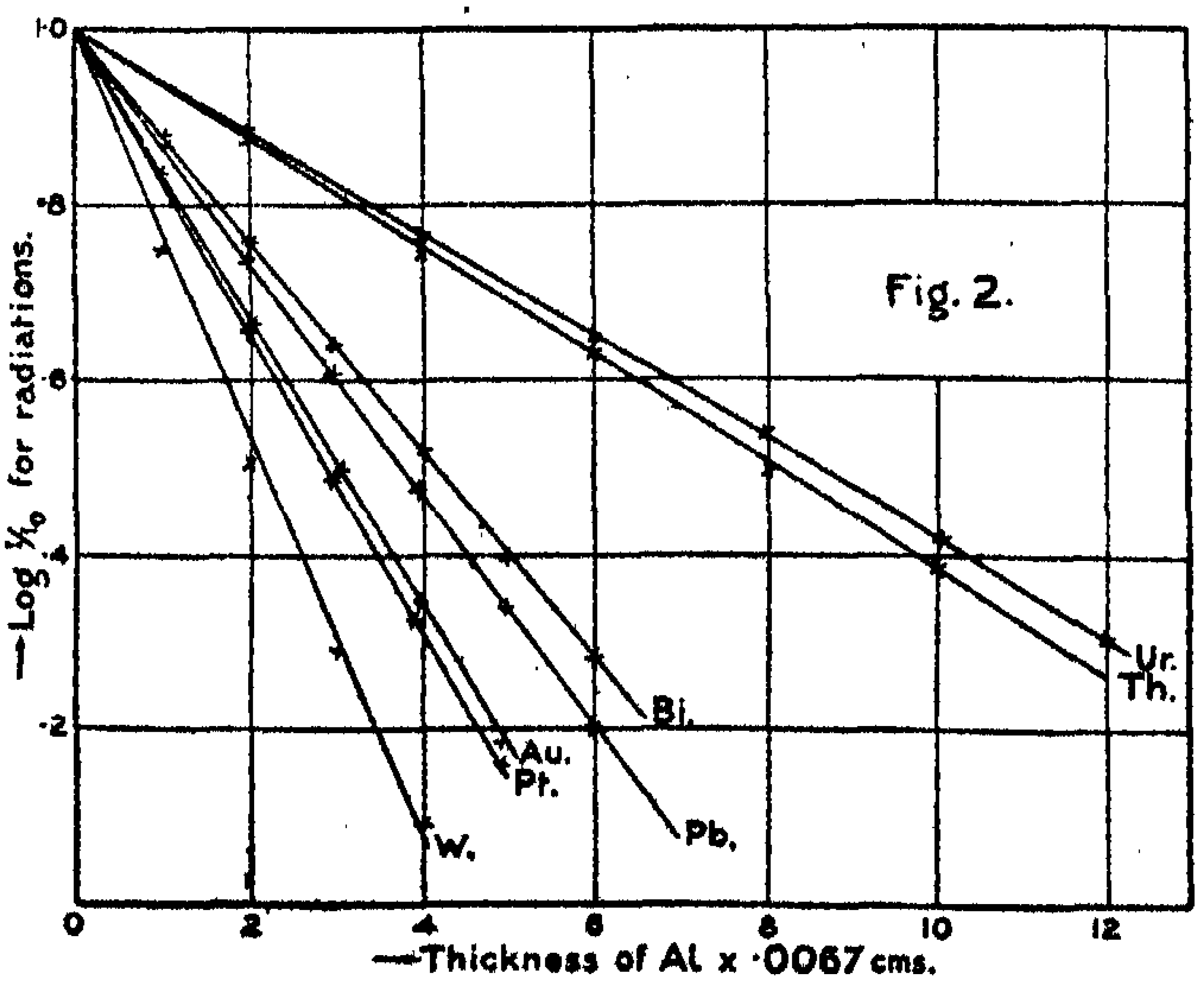

Fig. 2.

Relation between the Atomic Weights of Elements Emitting same Characteristic Radiation.

If a curve be plotted with λ/ρ for ordinate and atomic weight as abscissa for these elements, it will be seen that the points so obtained lie on an approximately smooth curve.

The determination of the values of λ/ρ for so many elements in Group L has revealed an interesting relation, similar to that pointed out by Whiddington,* between the atomic weights of two elements which, though belonging to different groups, can be caused to emit the same characteristic radiation. If W_L represents the atomic weight of an element in Group L that gives out a radiation having a certain penetrating power as measured by the λ/ρ in aluminium, and W_K is the atomic weight of an element in the first group (K), which, if it existed, would give out the same radiation (this is obtained from the curve mentioned at the commencement of the paper), then it will be found that in all cases the relation between W_L and W_K is expressed almost exactly by the empirical formula—

$$W_K = \tfrac{1}{2}(W_L - 48).$$

This is shown for all elements from tungsten to uranium in the following table, which explains itself:—

Element in second group (Group L).	λ/ρ.	Atomic weight of element in Group L, W_L.	Atomic weight of element in Group K, which, if it existed, would emit the same characteristic radiation.	
			Value from curve, experimental.	Value calculated from formula $W_K = \frac{1}{2}(W_L - 48)$.
Tungsten	30·0	184·0	69·7	68·2
Platinum	22·2	195·0	75·2	73·5
Gold	21·6	197·2	75·5	74·6
Lead	17·4	207·0	79·8	79·5
Bismuth	16·1	208·5	80·7	80·2
Thorium	8·0	232·0	91·4	92·0
Uranium	7·5	238·0	93·2	95·0

It is impossible, at present, to state what is the physical significance of this formula, but it is most useful in determining the absorption coefficients of elements directly from their atomic weights.

Selective Absorption by Elements of Group L.

The elements belonging to Group K exhibit another leading characteristic. This is that any particular element in Group K shows a selective absorption for radiations which have a penetrating power just greater than its own. Thus if the coefficient of absorption of an element X in Group K, such as copper, be measured for the various homogeneous beams from calcium to cerium, when the radiation absorbed is soft the absorption in X is considerable, but as the radiation is made more penetrating the absorption in aluminium and in the element X diminishes proportionately. When, however, the radiation which is being absorbed is made more penetrating than the secondary characteristic of the metal X, the absorption in X first ceases to diminish as rapidly as the absorption in aluminium, then it increases, and it is at this point of increase that the characteristic radiation of the element X is excited. As the primary beam becomes still more penetrating, the absorption in the element X begins to diminish, and eventually the absorptions in aluminium and the metal X diminish proportionately.

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* 'Nature,' November 30, 1911.

In order to show that the same phenomena take place with the elements of Group L, the absorption of thin layers* of lead oxide and bismuth carbonate for a series of homogeneous beams belonging to Group K was measured. The percentage absorptions by the thin layers of the two salts were determined for the characteristic radiations from copper, zinc, arsenic, selenium, bromine, strontium, molybdenum, silver, and tin. It was impossible to use the pure elements lead and bismuth, owing to the difficulties of obtaining thin enough layers for absorbing sheets. On this account only relative values of the absorption coefficients have been determined, but these serve to show all that is necessary.

In the following tables the first column shows the radiation absorbed, the

Absorption by Lead Oxide.

Secondary radiator.	Absorption in Al. Absolute λ/ρ.	Absorption in Pb. $k\,(\lambda/\rho)$.	$\frac{\text{Absorption in Pb}}{\text{Absorption in Al}}$, $= k^{-1}$ times value below.
Copper	47·7	269	5·6
Zinc	39·4	224	5·7
Arsenic	22·5	140	6·2
Selenium	18·9	129	6·9
Bromine	16·3	126	7·7
Strontium...........	13·0	161	12·4
Molybdenum	4·7	143	30·0
Silver	2·5	84	34·0
Tin	1·57	63	40·0

k is of the order unity.

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* These layers were made by mixing the salt in question with a small amount of pure gum; the absorption of a thin layer of the paint so formed was then measured. In this way it was impossible to obtain exactly even thicknesses of the salt, so that an error is

Absorption by Bismuth Carbonate.

Secondary radiator.	Absorption in Al. Absolute λ/ρ.	Absorption in Bi, relative. $k'(\lambda/\rho)$.	$\frac{\text{Absorption in Bi}}{\text{Absorption in Al}}$, $= k'^{-1}$ times value below.
Copper	47·7	277	5·8
Zinc	39·4	238	6·0
Arsenic	22·5	152	6·8
Selenium	18·9	134	7·0
Bromine	16·3	117	7·0
Strontium	13·0	165	12·7
Molybdenum	4·7	147	31·3
Silver	2·5	87	34·9
Tin	1·57	66	42·0

k' is of the order unity.

second the absorption in aluminium for this radiation, the third the relative absorption in the salt.

The two following curves show graphically the relation between absorption in aluminium and the relative absorption in lead and bismuth. The

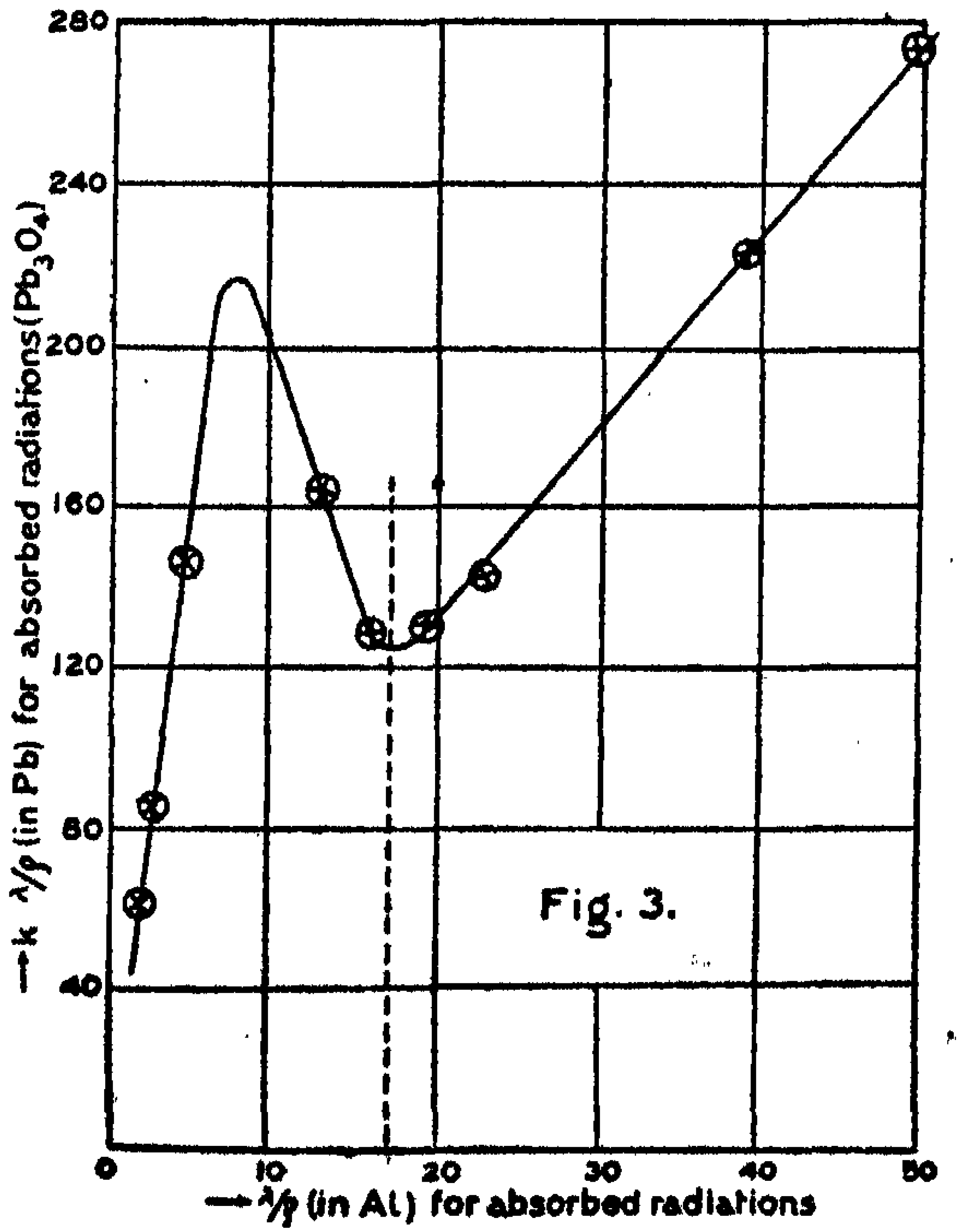

Fig. 3.

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introduced in the determination of λ/ρ. Owing to this, no correction has been applied for any slight lack of homogeneity of the rays from the several elements which served as radiators.

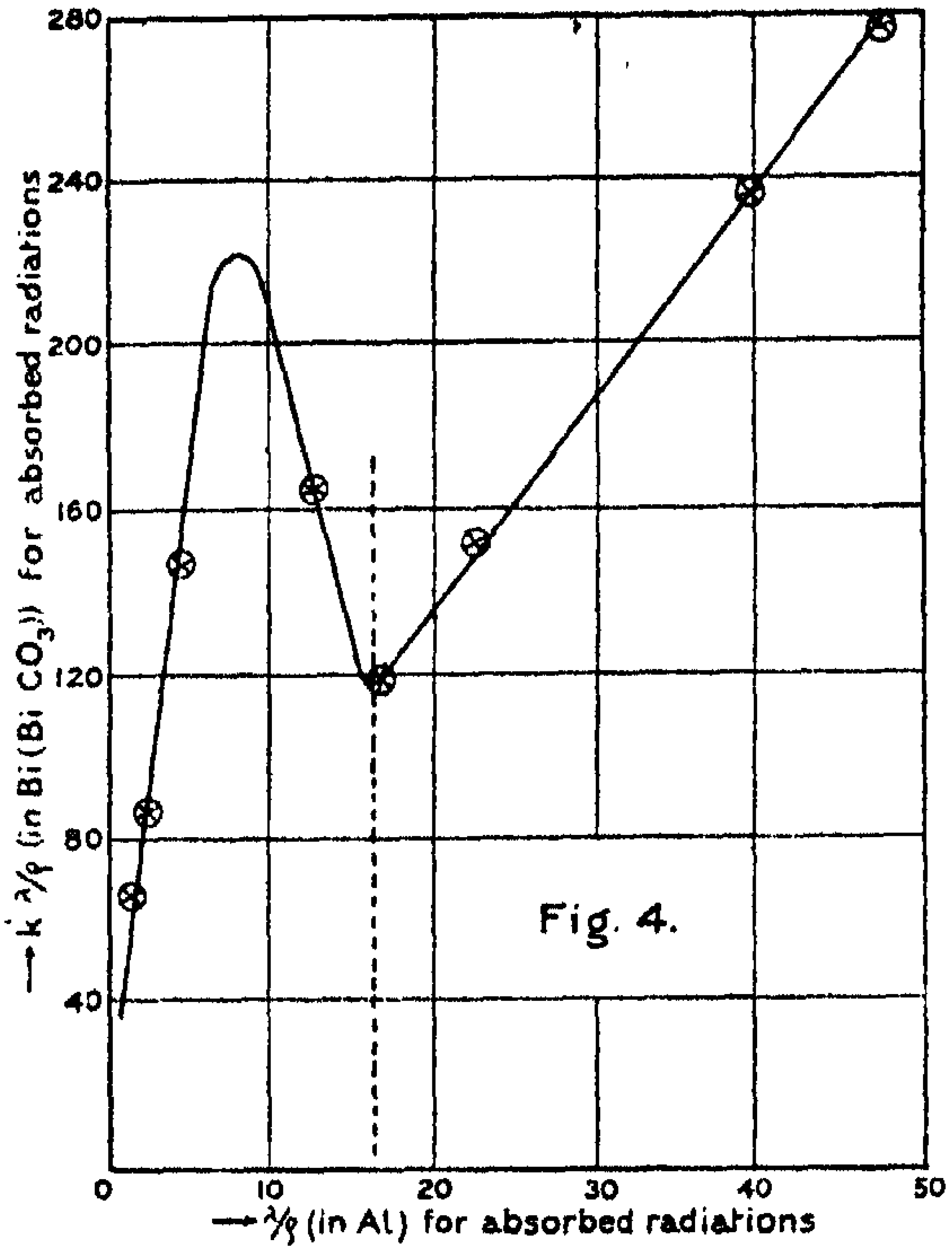

Fig. 4.

absorption by the light elements in the two salts is practically negligible when the relation between the relative masses and the absorption coefficients of the light and heavy elements are considered, so that the values obtained show within the limits of error of the experiment the absorption in lead and bismuth.

It will be seen that the shape of both curves is similar in its general features to that obtained for elements of Group K. In these curves the dotted lines show the point at which the characteristic radiation is excited. This can be found directly from the known values of λ/ρ for the homogeneous radiations from lead and bismuth, or it can be calculated from the empirical formula. The results demonstrate that the lead radiation ($\lambda/\rho = 17{\cdot}4$) is excited between the elements selenium ($\lambda/\rho = 18{\cdot}5$) and bromine ($\lambda/\rho = 16{\cdot}4$), whereas bismuth ($\lambda/\rho = 16{\cdot}1$) is excited between bromine ($\lambda/\rho = 16{\cdot}3$) and strontium ($\lambda/\rho = 13$). Thus these elements of Group L exhibit the same absorption phenomena as elements of Group K, in so far as they need a more penetrating radiation than themselves to be the exciting source.

Summary.

The results of these experiments show that there is a whole group of elements (Group L), containing tungsten, gold, platinum, bismuth, and the radioactive elements thorium and uranium, which emit when suitably excited secondary homogeneous Röntgen radiations similar in type to those emitted by the elements of the ordinary Group K. Their homogeneity has been demonstrated by a method which allows the scattered radiation to be subtracted. The values of the absorption coefficients in aluminium have been determined.

An empirical relation exists between atomic weights (W) of two elements which are in different groups, but which give out the same characteristic radiation. It is expressed by the formula

$$W_K = \tfrac{1}{2}(W_L - 48).$$

This relation holds for all the elements in Group L within the limits of experimental error.

It has also been shown that the elements of Group L exhibit the same selective absorption phenomena in the neighbourhood of an absorption band. The values given are for lead and bismuth. These results would go to show that the mechanism of production and the type of the radiations of both groups are the same, but further experiments are still necessary to show that there is an exact similarity.

In conclusion my best thanks are due to Prof. Sir J. J. Thomson for his kind interest in these experiments.

On the Variation of the Resistance of Selenium with the Voltage.

By E. E. Fournier d'Albe, B.Sc., A.R.C.S., Assistant Lecturer in Physics in the University of Birmingham.

(Communicated by Prof. J. H. Poynting, F.R.S. Received February 9,—Read March 7, 1912.)

That the conductivity of selenium depends not only upon the illumination but also upon the voltage applied to it was discovered in 1875 by W. G. Adams,[*] and the fact that the selenium preparation examined by Adams had a positive temperature coefficient of resistance made it very improbable that the effect was due to Joulean heat.

G. M. Minchin,[†] using aluminium electrodes, found that the conductivity increased nearly fourfold on increasing the voltage from 2 to 12 volts, and that it was approximately proportional to the voltage.

J. Luterbacher,[‡] in the course of a special study of this "potential effect" ("Spannungseffekt"), found that it is greater for direct currents than for alternating currents of the same energy, that the curve exhibiting the resistance in terms of the voltage is (approximately) parabolic, and that the potential effect cannot be explained by Joulean heat.

F. C. Brown[§] studied the potential effect in a Ruhmer "cell" and a Giltay "cell," and found that the conductivity varies by an amount which in the Ruhmer "cell" is almost proportional to the voltage, while in the Giltay "cell" the variation decreases as the voltage is increased.

C. Ries,[||] using carbon filament electrodes embedded in slate, obtained increases in the conductivity of selenium ranging from 5 to 50 per cent. on increasing the voltage from 0·4 to 4 volts, but the figures given are insufficient to determine the relation between voltage and conductivity. Some further work by the same author is dealt with below.

The present work was undertaken with the object of discovering the relation between voltage and conductivity, and of throwing some further light on the nature of the potential effect.

It is necessary to prefix some definitions.

The Selenium Bridges.—The term "selenium cell" should be restricted, according to Minchin, to the electrolytic cells in which the incident light produces an E.M.F., and not a change of resistance. Such real cells were devised by Sabine in 1878, and improved forms were used by Minchin for the electrical measurement of starlight.[*] Those selenium preparations, on the other hand, in which the light is used to effect a change in the resistance, Minchin very appropriately calls "selenium bridges," and I propose to adopt this term for all such preparations.

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[*] 'Roy. Soc. Proc.,' 1875, vol. 23, p. 535.

[†] 'Roy. Soc. Proc.,' 1908, A, vol. 81, p. 9.

[‡] 'Ann. der Physik,' 1910, vol. 33, p. 1392.

[§] 'Phys. Rev.,' July, 1911, vol. 33, p. 1.

[||] 'Physikal. Zeitschr.,' July 1, 1911, vol. 12, p. 529.

The Potential Effect.—In all dry selenium bridges, an increase of voltage always produces an increase in the electrical conductivity. This, for reasons which will presently appear, is best expressed as a diminution of resistance. If R_0 is the resistance of a selenium bridge at an infinitesimal voltage, and R_V its resistance at a voltage V, then $(R_0-R_V)/R_0$ is the "potential effect" on the resistance of the bridge in question, or, shortly, the "potential effect." (This must be distinguished from what may be called the "photo-voltaic effect" in electrolytic selenium cells, or the production of an E.M.F. by light. The literal translation of "Spannungseffekt" = "tension effect" is obviously open to misinterpretation, and "voltage effect" is perhaps too suggestive of the "Volta effect" of contact electrification.)

The Coefficient of the Potential Effect.—The main result of the present work is to show that *the potential effect is proportional to the logarithm of the voltage*, in all selenium bridges having graphite electrodes, and for all voltages above 1 volt. This is expressed by the equation

$$\frac{R_1-R_V}{R_1} = F \log V,$$

where R_1 is the resistance at 1 volt and F is a constant for a given bridge under the same conditions as to temperature, illumination, and fatigue.

Method.—Some 70 different selenium bridges were prepared, some of the Shelford-Bidwell type, but most of them by a new method as follows:—Square plates of a highly-insulating unglazed porcelain, 5 cm. wide and 3 mm. thick, were coated on one face with soft graphite. This face was then divided into two separate conducting portions as shown in fig. 1, the to-and-fro separating line being drawn with a diamond. The plate so prepared then received a coating of selenium, either by spreading molten selenium over it with a glass or iron spatula, or by exposing it to a current of selenium vapour. After cooling rapidly, the selenium was sensitised in the usual way by prolonged exposure to a temperature of 200° C.

Three different varieties of stick selenium were used, one of them obtained from Kahlbaum, Berlin, and two others of unknown origin. No special purification was attempted, but as the results did not vary systematically from one specimen to another, nor with the mode of preparation, the conclusions of this paper are not likely to be affected by whatever slight impurities the selenium contained.

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[*] 'Roy. Soc. Proc.,' 1895, vol. 58, p. 142; and 1896, vol. 59, p. 231.

A few bridges were also prepared by coating the porcelain with a thin layer of selenium in the first instance, and then drawing on the annealed selenium a pattern of thick pencil lines interlaced as above. These bridges had a high resistance, combined, as a rule, with a high sensitiveness to light. But the potential effect showed no marked variation from that observed in the first type.

The lowest temperature used was that of liquid oxygen (−182° C.) and the highest 100° C. All the bridges examined had a negative temperature coefficient of resistance at ordinary temperatures.

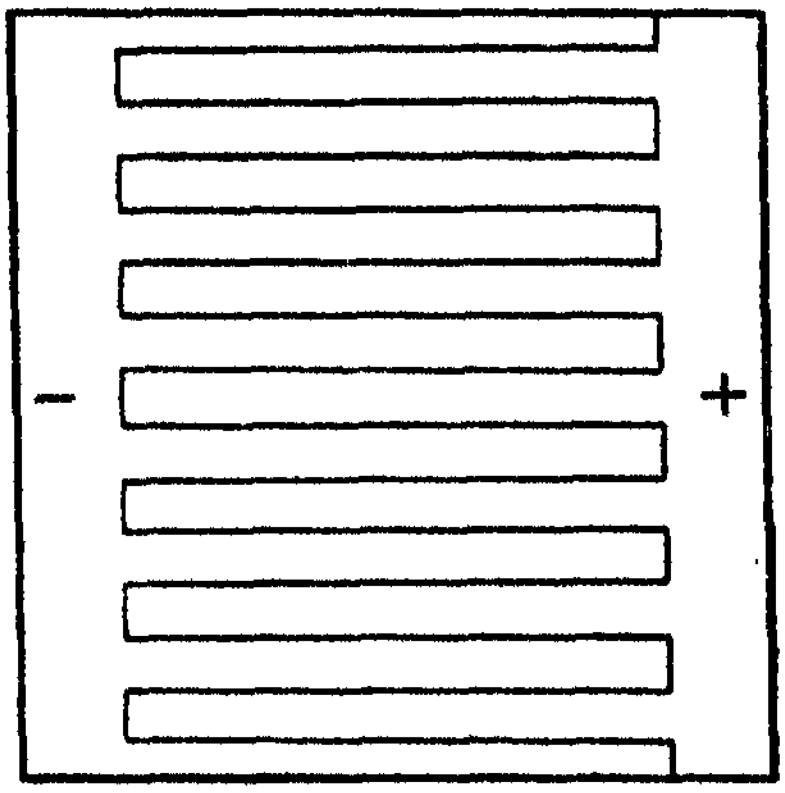

Fig. 1.

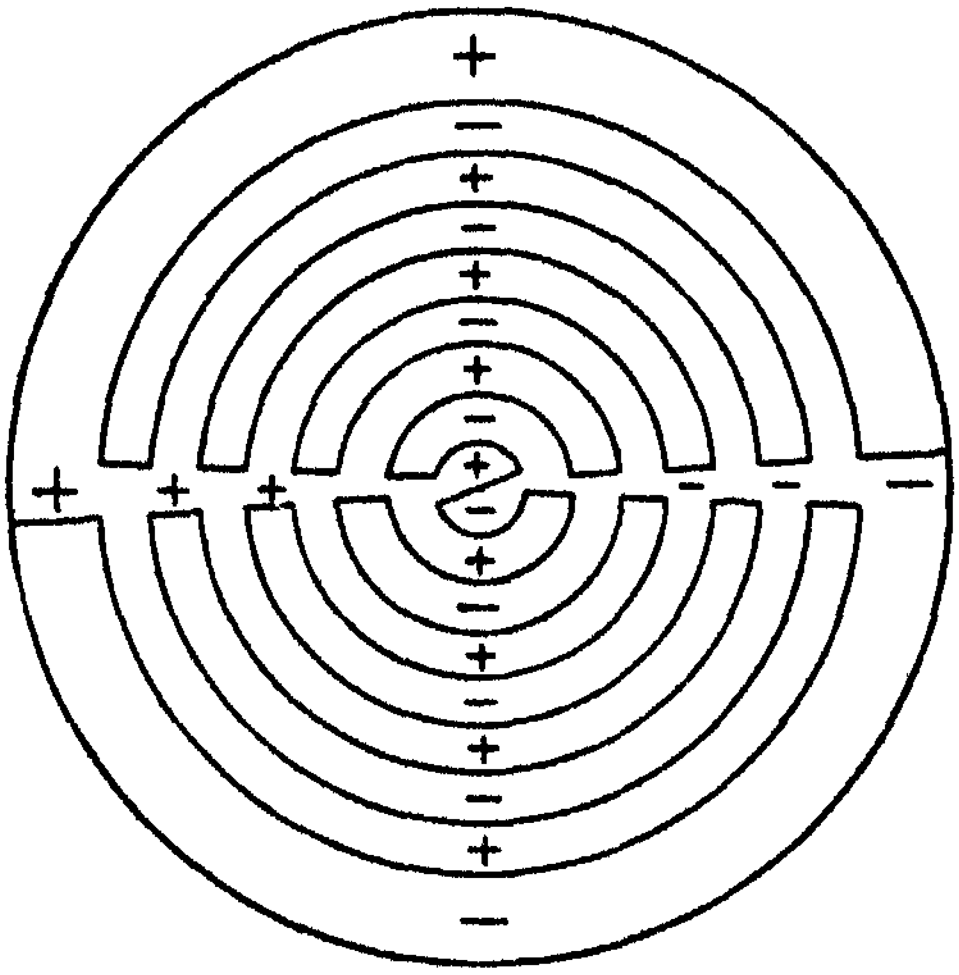

Fig. 2.

In addition to the graphite-selenium bridges, a platinum-selenium bridge, purchased from Presser, Berlin, was studied. It has a circular active surface 4·5 cm. in diameter. From an inspection of this bridge it appears that platinum is deposited upon an insulating surface, and circular concentric lines are ruled in it as shown in the diagram (fig. 2). Selenium is then spread over the whole surface. In the actual bridge there are 40 circles 0·5 mm. apart.

Measurements.—A Wheatstone bridge arrangement is unsuitable, as the voltage applied to the selenium is not necessarily proportional to the voltage used. A substitution method was therefore used throughout. The bridge under examination was put in circuit with a battery and an Ayrton-Mather moving-coil mirror galvanometer giving 6 mm. of a deflection per micro-ampère on a scale 1 m. away. (For measuring the smallest currents, a Broca galvanometer giving a deflection of 4 mm. for 10^{-9} ampère was substituted.) The scales of both galvanometers were carefully calibrated.

The voltage was applied for one minute and then reversed. Readings were taken after one minute in each direction. The two readings were, as a rule, sensibly the same if the bridge had been carefully dried and was protected from moisture, by varnishing or otherwise. The reversal not only tests for polarisation, but enables the bridge to assume the resistance appropriate to the voltage—a point to be borne in mind when testing the voltage law above set forth.

A set of manganin resistances was then substituted for the selenium bridge. The set consisted of 10 coils of 0·1 megohm each, 10 of 0·01 megohm each, and 10 of 0·001 megohm each. The resistance was adjusted to the nearest 1000 ohms, so as to approach as closely as possible to the mean reading for the selenium bridge.

The deflections obtained with the manganin and the selenium respectively (corrected, if necessary, for scale error) were then taken as inversely proportional to their respective resistances.

E.M.F.'s up to 20 volts were obtained from Clark cells, Daniell cells, or small accumulators, whose E.M.F. was compared with that of a Clark cell. Higher voltages were obtained from a set of accumulators capable of yielding up to 800 volts in steps of 20 volts. In using the latter, the voltage was controlled by means of a set of three Kelvin electrostatic voltmeters arranged in parallel across the terminals.

Results.—The logarithmic law was found to hold in *all* the bridges examined, and was, in one instance, verified for a voltage as high as 220. Fig. 3 shows a typical set of readings obtained with the Presser bridge (No. 1) without reversing the current. It will be seen that the resistance oscillates in small jerks about the straight line representing the logarithmic law. These jerks are smoothed out by one or more reversals. The resistance in this case is governed by the relation

$$\begin{aligned} R_V &= (225{,}000-38{,}000\log_{10}V)\text{ ohms} \\ &= 225{,}000\,(1-0{\cdot}169\log_{10}V)\text{ ohms.} \end{aligned}$$

The factor 0·169 appearing in the brackets is the "coefficient of the voltage effect," denoted above by F.

Another set of results, obtained with the Presser bridge after further repose in the dark, is embodied in the following table.

V.	log V.	Δ log V.	R_V.	ΔR.	ΔR/Δ log V.
1·43	0·155	—	252,500	—	—
4·78	0·675	0·519	230,000	22,500	43,300
9·46	0·976	0·820	217,000	35,500	43,300
14·19	1·152	0·996	209,500	43,000	43,200

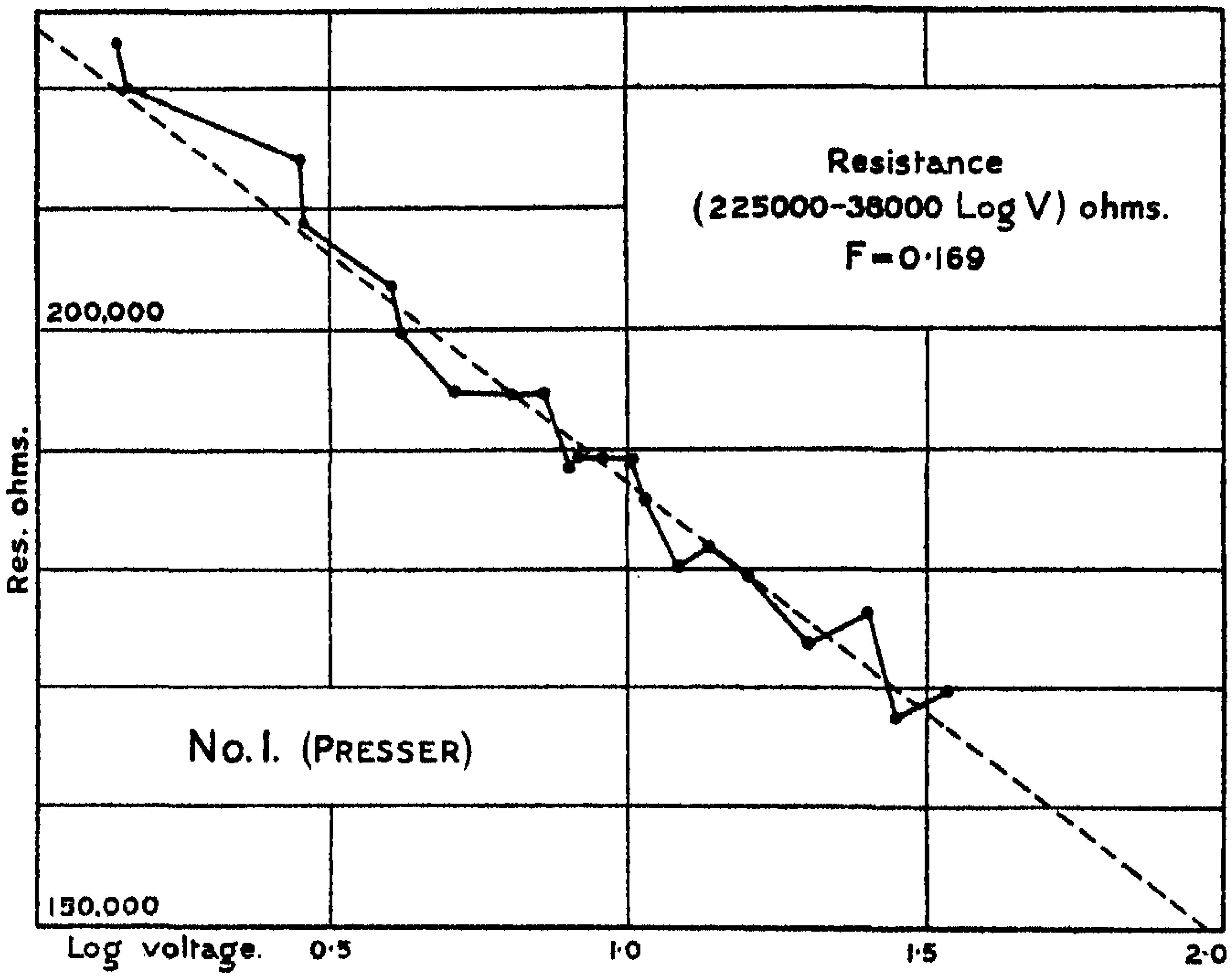

Fig. 3.

The coefficient F is calculated from any two values of the resistance by means of the formula

$$F = \frac{R_V - R_v}{R_V \log v - R_v \log V},$$

where V and v are the two voltages and R_V and R_v the corresponding resistances. The mean value of F from the above table is 0·167.

After a fortnight's repose, the same Presser bridge showed a resistance as high as 339,000 ohms at 1 volt, and a decrease of 56,350 ohms for Δ log V = 1. This gives F = 0·167, as before.

When illuminated by an incandescent gas lamp giving an intensity of 16 metre-candles, the Presser bridge showed a resistance governed by the relation $R_V = (80{,}500 - 12{,}500 \log V)$ ohms, which gives F = 0·155. From this it was at first thought that F is diminished by white light, but subsequent experience showed that it is sometimes increased.

It may also be stated here that there was no systematic difference between white light and monochromatic light. Thus, a bridge covered with two plates of ruby glass behaves, as far as the potential effect is concerned, as if it were illuminated with white light containing about the same amount of red light. As the potential effect occurs also in forms of selenium which are quite insensitive to light, and even in a solid selenium stick, no special study was made of the colour or even the intensity of the light used, the object being merely to test the validity of the logarithmic law for various kinds and intensities of illumination taken at random. And the result was in each case a confirmation of that law.

A selenium-graphite bridge (No. 2), made by smearing selenium over graphite, was examined in darkness, in diffused daylight, in gaslight, and in sunlight; also in liquid air, at 13° C., and at 44° C. Its resistance at 1 volt ranged from 16,000 to 32,000 ohms. The constant F had a mean value of 0·318. It was 0·278 in the dark at 44° C., 0·385 in sunlight at 13° C., and 0·344 in liquid air and dull daylight. The effect of liquid air was to double its resistance while immersed, and to produce a subsequent gradual increase of the resistance to about three times its original amount. This may be connected with the fact that a selenium stick, immersed in liquid air, becomes very brittle and friable.

The behaviour of a bridge (No. 3) similarly made is shown by fig. 4. The resistance R_1 ranged from 39,600 to 8200. The letters indicate the separate series of measurements. The values of F are given by the following table:—

a. Dark	0·278	*e.* Dark	0·290
b. 12 metre-candles	0·274	*f.* Dark	0·276
c. Dark	0·283	*g.* Dark	0·271
d. Dark	0·272	*h.* 12 metre-candles	0·281

The mean value of F is 0·278. If it were the same for all the series, the lines would all intersect in the axis of abscissæ at a point representing 4000 volts.

Curve *j* shows the gradual inception of the potential effect below 1 volt.

Another bridge, which I shall call No. 4, was made by tracing pencil lines on selenium. Its resistance at 1 volt varied very widely, even in the dark. The extreme values were 8·15 megohms and 1·64 megohms in the dark, the former after prolonged repose. The corresponding values of F were 0·190 and 0·232. In sunlight R_1 was 188,000 ohms, and F was 0·157. In spite of these considerable variations of F from one series of measurements to another, the logarithmic law applied very rigidly to any given series, the maximum deviation from it being 0·3 per cent. This is specially valuable inasmuch as the voltage varied from 1 to 100 volts. (For the very high resistances a method of comparative deflections had to be used.)

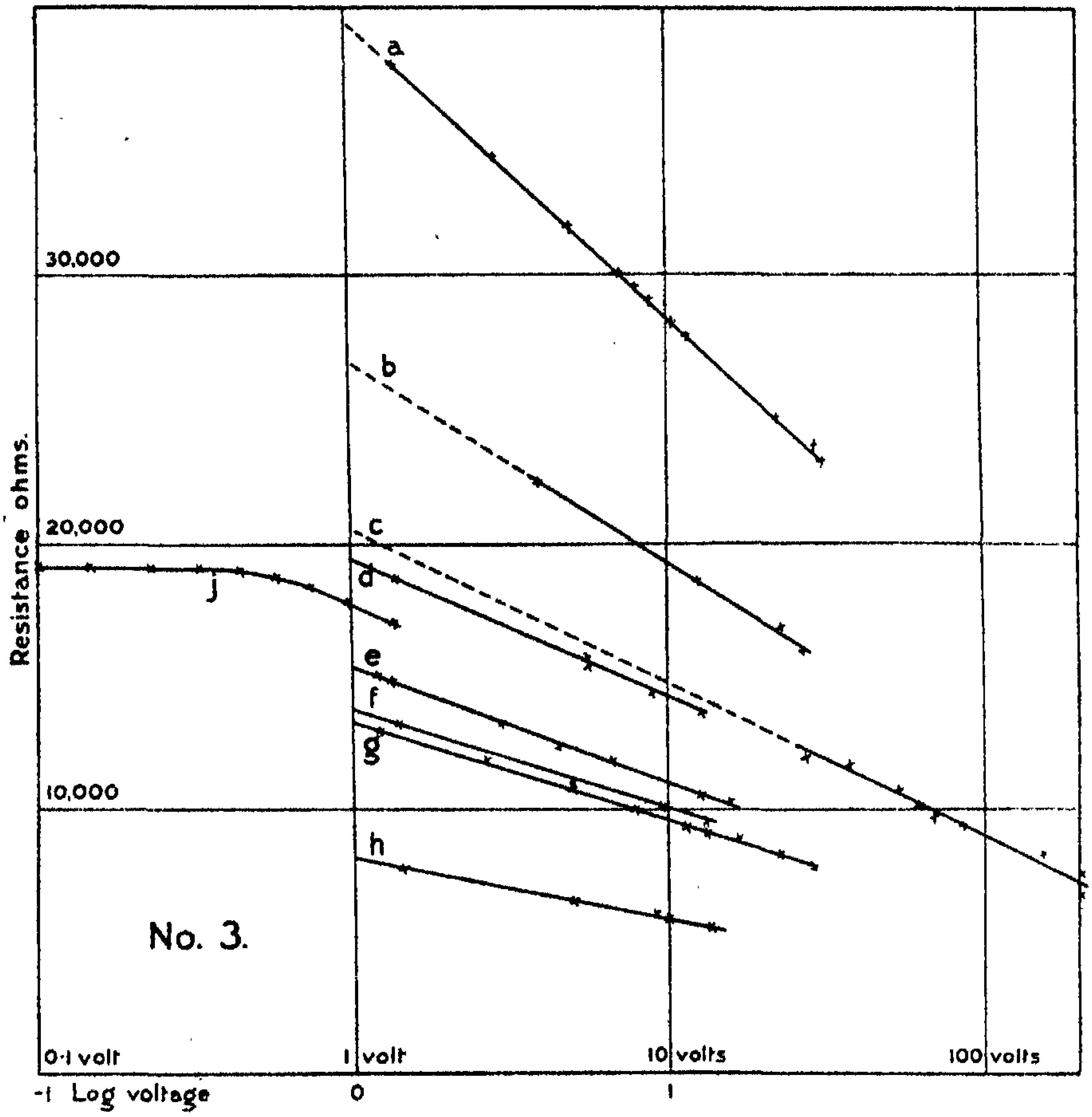

Fig. 4.

No. 5 was a single selenium line between two graphite lines, the gap being 0·5 mm. wide, and the selenium 0·1 mm. thick. The following table gives the values of R_1 (in megohms) and F for six different series of measurements, the highest voltage being 24 volts:—

	R_1.	F.		R_1.	F.
a. At 15° C., dark	3·7	0·33	*d.* At −180° C., daylight	12·2	0·35
b. At 15° C., daylight ...	1·95	0·41	*e.* At −180° C., long daylight	11·2	0·34
c. At −180° C., daylight	20·3	0·42	*f.* At −180° C., long dark......	23·4	0·34

It will be seen that, although R_1 varies 1100 per cent., F only varies 27 per cent. from one series to another.

No. 6 was a bridge formed with selenium vapour, deposited on graphite and annealed. Its resistance was only some 3000 ohms. F was 0·190 in the dark, and 0·193 in gaslight (12 m.c.). No. 7 was made by the same process, but had a thinner film, a higher resistance (R_1 = 512,000 ohms), and a greater sensitiveness to light. The mean value of F was 0·26.

The above are a few typical results obtained by me, out of a larger number of series of measurements, all of which pointed to the same conclusion: that the reduction of the resistance is, under conditions otherwise constant, proportional to the logarithm of the voltage (above 1 volt). But F may vary considerably (as much as 30 per cent.) in the same bridge under different conditions of illumination, temperature, and fatigue.

Results of other Observers.—The behaviour of the Giltay "cell," studied by Brown,* confirms in general the logarithmic law, whereas the Ruhmer "cell" does not. But the Giltay bridge shows evident traces of polarisation, which are carefully eliminated from my measurements, and the cases are therefore not comparable.

A Ruhmer bridge also figures in Luterbacher's work,† and on plotting R against log V (abscissæ), a curve is obtained having a very perceptible concavity towards the axis of abscissæ. On the other hand, the figures given for a bridge of the Shelford-Bidwell pattern (p. 1406) under 15, 30, 45, 60, and 125 volts show a satisfactory agreement with the logarithmic law.

I have had no opportunity of examining a Ruhmer bridge, and cannot form any opinion as to the circumstances which cause its deviation from the logarithmic law. But it is evident that bridges made with metallic wires are less likely to yield simple relations than bridges made with carbon, which has no chemical action on selenium.

Quite recently, Ries‡ has carried out a special investigation of the potential effect in selenium and antimonite, without, however, discovering any simple relation between voltage and resistance. The potential effect was observed in a selenium bridge having a positive ("metallic") temperature coefficient of resistance, and Joulean heat is therefore excluded as a cause. The effect is extremely small (F = about 0·03) between 2 and 12 volts, but appears to obey the logarithmic law. At 55 volts and 110 volts the resistance falls very considerably, probably owing to the heating of the support, which was embedded in paraffin. The support was presumably slate, as in Ries's previous experiments, but no information is given on this important point.

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* *Loc. cit.*, p. 21.

† *Loc. cit.*, p. 1400.

‡ 'Ann. der Physik,' December, 1911, vol. 36, p. 1055.

Theoretical.—The strongest argument against the possibility of the potential effect being due to Joulean heat advanced by Luterbacher is that a direct current and an alternating current of the same heating power produce very different potential effects, the D.C. effect being about three times the A.C. effect. But it can also be eliminated by calculating the Joulean heat from the current and resistance, and the rise of temperature from these and the surface and emissivity of the wire. The rise of temperature θ is given by the equation

$$\theta = \frac{0{\cdot}239\,\mathrm{V}^2}{h\mathrm{AR}_0(1-\alpha\theta)} = \frac{0{\cdot}239\,\mathrm{V}^2}{h\mathrm{AR}_0}\left(1+\frac{\alpha\,0{\cdot}239\,\mathrm{V}^2}{h\mathrm{AR}_0}\right), \text{ approximately,}$$

where V is the voltage, h the emissivity, A the area, α the temperature coefficient of resistance, and R_0 the resistance at 0° C. under V volts. According to Glazebrook, Bousfield, and Smith,* h in metallic wires ranges from 0·037 to 0·088 cal. per sec. cm.^{2} deg. If it were 0·03 in the Presser bridge, then the rise of temperature at 10 volts in the dark would be 0·0002° C., whereas it would require a rise of some 5° C. to account for the observed 14 per cent. reduction of the resistance. Calculations with regard to other bridges show a similar disproportion, so that Joulean heat is excluded as a cause, unless the emissivity of selenium is 10,000 times smaller than that of metals. Control experiments showed that it cannot in any case be more than 100 times smaller.

This was confirmed by determining the resistance of a pencil line drawn on porcelain under various voltages. The resistance at 1 volt was 66,000 ohms. Exposure to 10 volts produced no measurable change in the resistance, even when prolonged for half an hour.

In the absence of a thermal explanation it becomes necessary to look for some other hypothesis. Luterbacher's "negative polarisation" is hardly adequate, as such a polarisation would itself be difficult to explain. Brown's interesting hypothesis of chemical instability is open to Ries's objection that all chemical processes are linked to definite temperatures, whereas both the sensitiveness and the potential effect in selenium are nearly the same in liquid air as at ordinary temperatures. Ries's sketch of an electronic theory seems the most promising line of investigation, and it may not be very wide of the mark if we compare the conductivity of selenium to that of a gas, due to ionisation by collision modified by a subsequent recombination of the ions.

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* 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 541.

In the present uncertainty with regard to the mechanism of conduction in solids it would be premature to attempt a theory of the potential effect on these lines. But, on the other hand, the simple relation between voltage and resistance specified above may furnish some guidance in a future choice among theories of conduction.

In conclusion, I have to thank Prof. Poynting for offering me ample facilities in conducting this investigation, and Prof. T. Turner for some valuable hints regarding the distillation of metals and the treatment of thin conducting films.

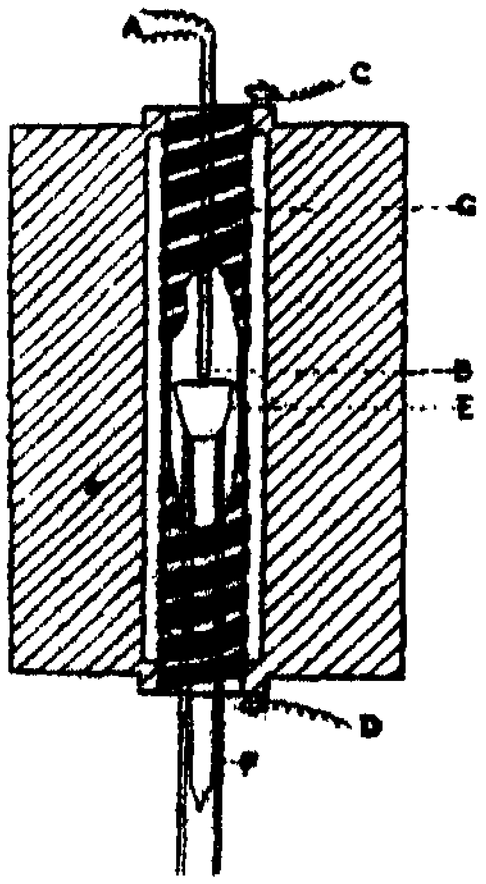
The Volatility of Metals of the Platinum Group.

By Sir William Crookes, O.M., For. Sec. R.S.

(Received February 15,—Read March 7, 1912.)

For the last two years I have been using an electric furnace, and some facts which came under my notice on the occasion of a breakdown of the heating arrangement led me to suspect that platinum was not so entirely fixed at temperatures well below its melting-point as has been universally accepted by chemists and physicists.

The electric resistance furnace used (fig. 1) is on the Heraeus system. It consists of a highly refractory porcelain tube, around which is coiled a ribbon of platinum foil, 11 mm. wide, 2·8 metres long, and 0·01 mm. thick,



A, Wires from thermo-junction.
B, Platinum platinum-rhodium junction.
C, D, Terminals of platinum strip.
E, Crucible.
F, Porcelain supporting tube.
G, Platinum strip.

Fig. 1.

each convolution almost, but not quite, touching its neighbour. The ribbon closely enwraps the tube, practically covering the surface to be heated, so that the heat produced by the passage of the electric current is immediately transmitted to the tube. The tube is 4 cm. internal diameter; the object to be heated stands on a porcelain rod fixed upright in the middle of the tube. The body of the furnace is made to slide up and down by means of a windlass, so as to allow the crucible to be properly adjusted. The temperature of the furnace is measured by a Le Chatelier platinum and platinum-rhodium thermo-couple.

Although the melting-point of platinum is 1753°,* it is not safe to use the furnace at higher temperatures than about 1500°, as a temporary variation in the voltage of the current for a few minutes, or a reduction of the resistance, may easily make a difference of one or two hundred degrees.

After a certain time the platinum ribbon coil gets thinner and melts at the weakest part, and the furnace becomes useless until a new porcelain tube and platinum ribbon coil are supplied. During the two years I have had the furnace in use this breakdown has happened three times.

On examining the point of rupture I was struck by the appearance of a fine glistening dust on the porcelain tube. I carefully removed particles to the slide of a microscope, and found the dust to consist of beautifully-formed hexagonal plates with a brilliant metallic lustre and perfect crystalline form. The amount at my disposal was infinitesimal—not more than a few milligrammes—and careful chemical examination showed me that the crystals were almost entirely platinum. A control examination by Messrs. Johnson and Matthey confirmed my observation. When the furnace was taken to pieces more crystalline deposits of platinum were found, especially inside the outer tube facing the platinum spiral. Fig. 2 shows some of these crystals.

At first sight it might seem superfluous to try experiments to see if platinum volatilised at all when strongly heated, considering how many generations of chemists have been daily igniting and weighing platinum crucibles. But it is customary among chemists to cleanse their crucibles between each using, and in some cases they are scoured with fine sand. It therefore seemed of interest to subject a platinum crucible to a temperature approaching that to which the platinum resistance coil had been exposed As an appreciable amount of platinum had sublimed and deposited in the form of crystals in the furnace it was possible that a carefully weighed platinum crucible exposed to a high temperature, after a certain number of hours, might show a detectable diminution in weight.

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* Waidner and Burgess, 'Bulletin of the Bureau of Standards, Washington,' 1907, vol. 3, p. 208.

I assumed that the loss of weight in a platinum crucible by sublimation, at temperatures not much above those available in chemical laboratories, would be very small, and would require the balance to be in the best condition to enable its indications to be relied on. The balance—a very delicate chemical one—I employed for this research was put into accurate adjustment, and not used for any other purpose. It was kept in a dry room at nearly constant temperature, and was locked when not actually in use. The grain* weights used were made for me in 1864 by Johnson and Matthey, and were turned out of bars of melted, cast, and well hammered platinum. They were adjusted by the method I described in the 'Chemical News' for April 19, 1867, and 'Phil. Trans. Roy. Soc.,' 1873, p. 288, and have been in use ever since.

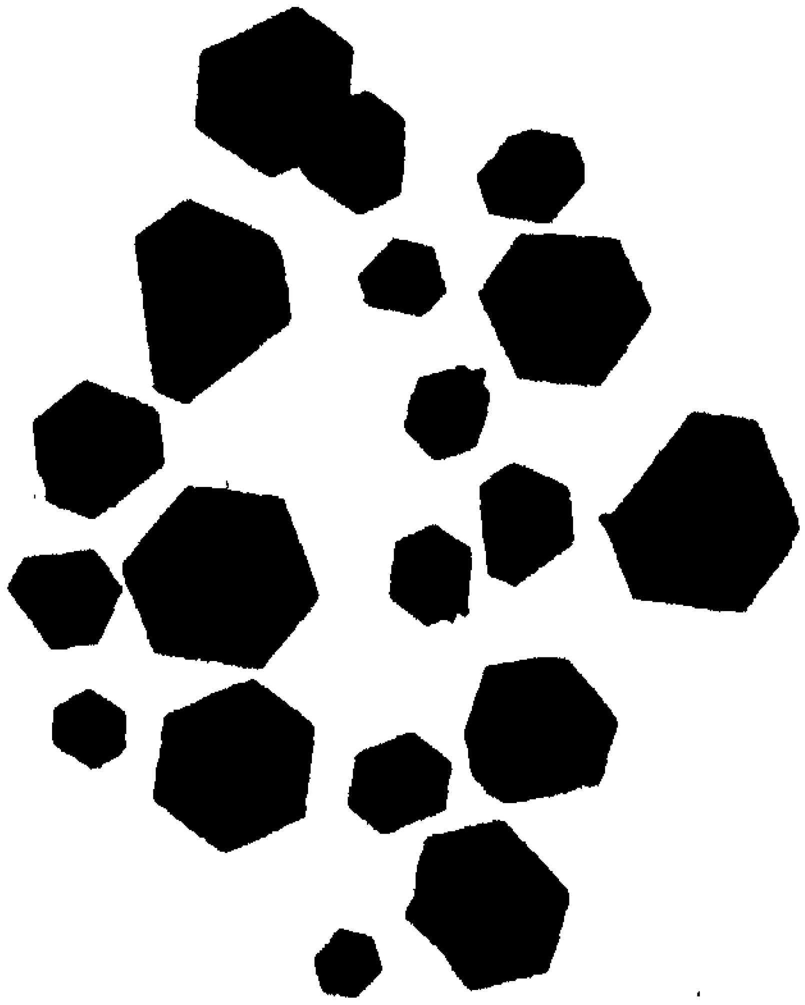

FIG. 2.

In 1895 Mr. Chaney, Superintendent of Weights and Measures, tested my 1000-grain platinum weight against their absolute standards, with the result that it was shown to be 3·9858 grains light. This made no difference to previous work with the weights, as in chemical operations the object is not to ascertain the absolute weight of a substance in terms of a grain or gramme, but to determine its relative weight in comparison with that which it possessed at some other time before submission to certain analytical or synthetical operations. If the weighings are performed with the same weights it does not matter whether they are absolutely of the value they profess to be—but it is of vital importance that they should bear a known proportion to each other.

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* My results are given in grains, not grammes. I have used my standard platinum grain weights for nearly fifty years, and they are too valuable to discard in favour of gramme weights, which would demand many months' work on them to bring them to the state of accuracy into which I have now got the grain weights.

On receiving Mr. Chaney's result I adjusted the 1000-grain weight by melting a bead of pure gold on it of the exact weight required, viz., 3·9858 grains, and then readjusted the whole series in the same way so as to get them absolutely as well as relatively accurate. In 1897, the readjustment being complete, I again asked Mr. Chaney to tell me the absolute weight of my platinum 1000 grains, and he returned it in a few days, saying that in air at 62° F. and pressure of 30 inches, my 1000-grain weight weighed 999·99574 grains, and *in vacuo* it weighed 999·90300 grains. Comparisons made last year showed that their values have remained absolutely unaltered, and I have the satisfaction of knowing they are as near perfection as can reasonably be expected.

By taking all precautions and using Gauss's method of interchanges, the balance will clearly indicate a difference of 0·0001 of a grain when loaded with 1000 grains in each pan. In the course of the research it was seen that this extreme delicacy was not needed, and, as weighing to such minute accuracy is very tedious, I have not, as a rule, gone beyond three places of decimals.

Platinum at 1300°.

A platinum crucible in good condition was ignited, cooled in a desiccator, and, an hour after, transferred to the balance. It weighed 150·487 grains. It was put into the electric furnace at 1300° C., and kept at that temperature for two hours. It was then removed, allowed to cool in a desiccator, and after another hour in the balance room it was found to weigh 150·458 grains, showing a loss of no less than 0·029 grain.

It was now put into the furnace for another two hours, and the temperature kept at 1300° (a white heat). On cooling an hour in the balance case its weight was found to be 150·427 grains. Table I shows the losses by sublimation when exposed to a temperature of 1300° for two hours at a time—being cooled and weighed between each heating. These results are shown plotted as a curve in fig. 3.

After this heating, and loss of 0·245 per cent. of its weight, the platinum crucible was not appreciably different in appearance from the time it was first put into the electric furnace. I examined its surface under the microscope, expecting to find the re-crystallisation described by Mr. Rosenhein.*

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* 'Roy. Soc. Proc.,' vol. 70, p. 252.

Table I.

	Grains.	Loss.	
		Grains.	Per cent.
Original weight of platinum	150·487	—	—
After 2 hours at 1300° weighed	150·458	0·029	0·019
„ 4 „ „	150·427	0·060	0·040
„ 6 „ „	150·394	0·093	0·062
„ 8 „ „	150·365	0·122	0·081
„ 10 „ „	150·344	0·143	0·095
„ 12 „ „	150·316	0·171	0·114
„ 14 „ „	150·295	0·192	0·128
„ 16 „ „	150·266	0·221	0·147
„ 18 „ „	150·233	0·254	0·169
„ 20 „ „	150·209	0·278	0·185
„ 22 „ „	150·194	0·293	0·195
„ 24 „ „	150·180	0·307	0·204
„ 26 „ „	150·159	0·328	0·218
„ 28 „ „	150·140	0·347	0·231
„ 30 „ „	150·118	0·369	0·245

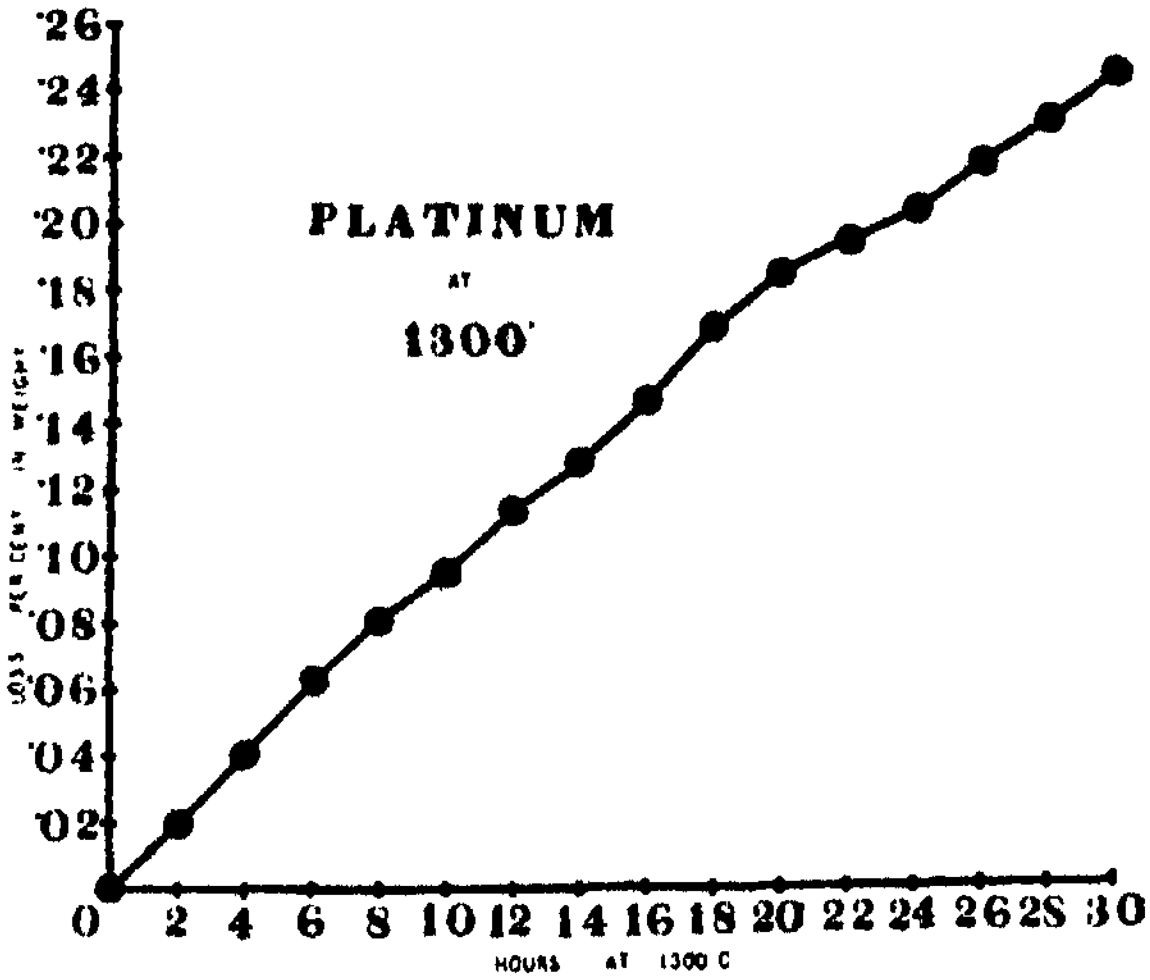

Fig. 3.

I was unable to detect any appearance resembling the photograph given in his paper. Probably the heating in his case was extended much beyond the 30 hours to which my crucible was exposed.

The action known as "air washing" (particles from a white-hot semi-molten surface being mechanically carried away by a current of impinging air) could not be active in the case of this experiment, for the tube of the furnace was closed at the top, nearly closed at the place where the crucible stood, and almost completely obstructed at the lower end. Therefore the platinum was in almost perfectly still air.

Palladium at 1300°.

Having with platinum obtained such unexpected results I tested palladium in similar conditions. The metal used was pure, in the form of thick plate, bright and polished on both sides.

In the following table it will be seen that, like platinum, palladium loses weight when exposed to a temperature of 1300° for two hours at a time, cooling and weighing at each interval:—

Table II.

	Grains.	Loss.	
		Grains.	Per cent.
Original weight of palladium	58·007	—	—
After 2 hours at 1300°, weighed	57·939	0·068	0·117
" 4 " "	57·883	0·124	0·214
" 6 " "	57·825	0·182	0·314
" 8 " "	57·808	0·199	0·343
" 10 " "	57·761	0·246	0·424
" 12 " "	57·735	0·272	0·469
" 14 " "	57·720	0·287	0·495
" 16 " "	57·702	0·305	0·526
" 18 " "	57·674	0·333	0·574
" 20 " "	57·656	0·351	0·605
" 22 " "	57·642	0·365	0·629
" 24 " "	57·624	0·383	0·660
" 26 " "	57·607	0·400	0·690
" 28 " "	57·591	0·416	0·717
" 30 " "	57·575	0·432	0·745

The curve plotted from these data is shown in fig. 4.

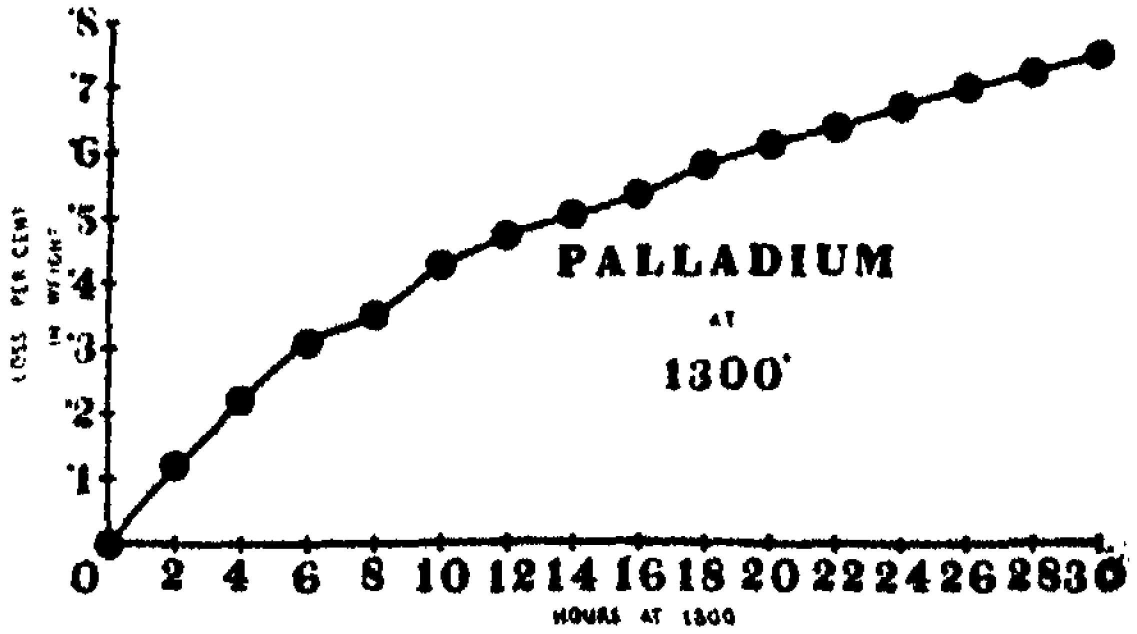

Fig. 4.

Moissan* says that "palladium is more easily fused than platinum, but is apparently less volatile." From the foregoing data it appears that at temperatures much below its melting-point palladium is three times as volatile as platinum.

At the end of the series the plate of metal had curved into an arc of about 60°, and its concave surface showed raised blisters. These blisters appeared after the first few heatings, and were due evidently to the liberation of occluded gas; further heating did not seem to increase the blisters. On examining the plotted curve the two-hourly loss of weight is seen to be greater in the earlier stages, diminishing up to 10 hours, and then pretty regular in a straight line. This agrees with the supposition that gas was given off during the earlier heatings, and the extra loss at these stages was due to the weight of gas liberated. From the above data the loss due to occluded gas would be about 0·15 of a grain, and supposing it were hydrogen it would measure about 111 c.c.

The bulk of 58 grains of palladium would be about 0·34 c.c., and as palladium will absorb more than 600 times its volume of hydrogen, the amount it could have held is 204 c.c.

As the heatings at 1300° progressed there was a gradual change in the surface of the metal from smooth to crystalline, and at the end of the 30 hours the surface had a crystalline moiré appearance, similar to that shown by iridium after similar heating, but not so marked, the crystals being smaller. The metallic appearance was unimpaired and no oxidation was detected on the surface.

Iridium at 1300°.

In May, 1908,† I suggested to chemists the great advantages of using crucibles of pure iridium instead of platinum in laboratory work. An iridium crucible is hard as steel; it may be heated for hours over a smoky Bunsen burner without injury. It will stand hours of boiling in aqua regia without appreciable attack; lead and zinc can be melted in it and boiled at a full red heat; likewise nickel, copper, gold, and iron can be melted in an iridium crucible, and poured out without injury. I used an iridium crucible for more than a year in the scandium research, and did not notice any appreciable diminution in weight. Any slight loss I attributed to mechanical abrasion during the cleaning and burnishing with sand, sometimes rendered necessary after an experiment.

Subsequent observations, however, led me to suspect that iridium was not altogether fixed at high temperatures; looking into the literature of the subject I met with several references to the supposed volatility of this metal. Accordingly, I commenced experiments to see if I could detect loss of weight in iridium at 1300°, a temperature at which I had found platinum to be slightly volatile.

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* 'Comptes Rendus,' January 22, 1906, vol. 143.

† 'Roy. Soc. Proc.,' A, vol. 80, p. 535.

An iridium crucible was heated for a few minutes in the electric furnace, and then cooled in a desiccator. It was taken to the balance room, put near the balance for an hour, and then placed on the pan. In an hour's time it was weighed and found to be 145·726 grains. This therefore was taken as the original weight from which to calculate the loss, if any, after long exposure to the high temperature of the furnace.

The crucible was put into the hot electric furnace, standing on an iridium plate, and kept at 1300° for two hours. It was then removed, allowed to cool with all precautions, when its weight was found to be 144·520 grains, showing a loss of 1·206 grains or about 0·8 per cent. The experiment was repeated until the iridium had been exposed to this temperature for a total of 22 hours.

The following table shows how in the above circumstances iridium loses weight, the data being plotted as a curve in fig. 5:—

Table III.

	Grains.	Loss.	
		Grains.	Per cent.
Original weight of iridium	145·726	—	—
After 2 hours at 1300°, weighed	144·520	1·206	0·828
" 4 " "	143·430	2·296	1·576
" 6 " "	142·208	3·518	2·414
" 8 " "	141·379	4·347	2·983
" 10 " "	140·354	5·372	3·686
" 12 " "	139·577	6·149	4·220
" 14 " "	138·605	7·121	4·887
" 16 " "	137·878	7·848	5·385
" 18 " "	137·151	8·575	5·884
" 20 " "	136·151	9·575	6·571
" 22 " "	135·092	10·634	7·297

Before the crucible was exposed to long continued heating to 1300° it was bright and polished. After four hours' heating it had a slightly crystalline look, which increased each time until, after 22 hours, the surface had assumed a beautiful moiré appearance.

After the iridium crucible had been heated in the electric furnace in the above experiments until it had lost 7·297 per cent. of its weight, it was submitted to further experiments to see if loss of weight was proportional to

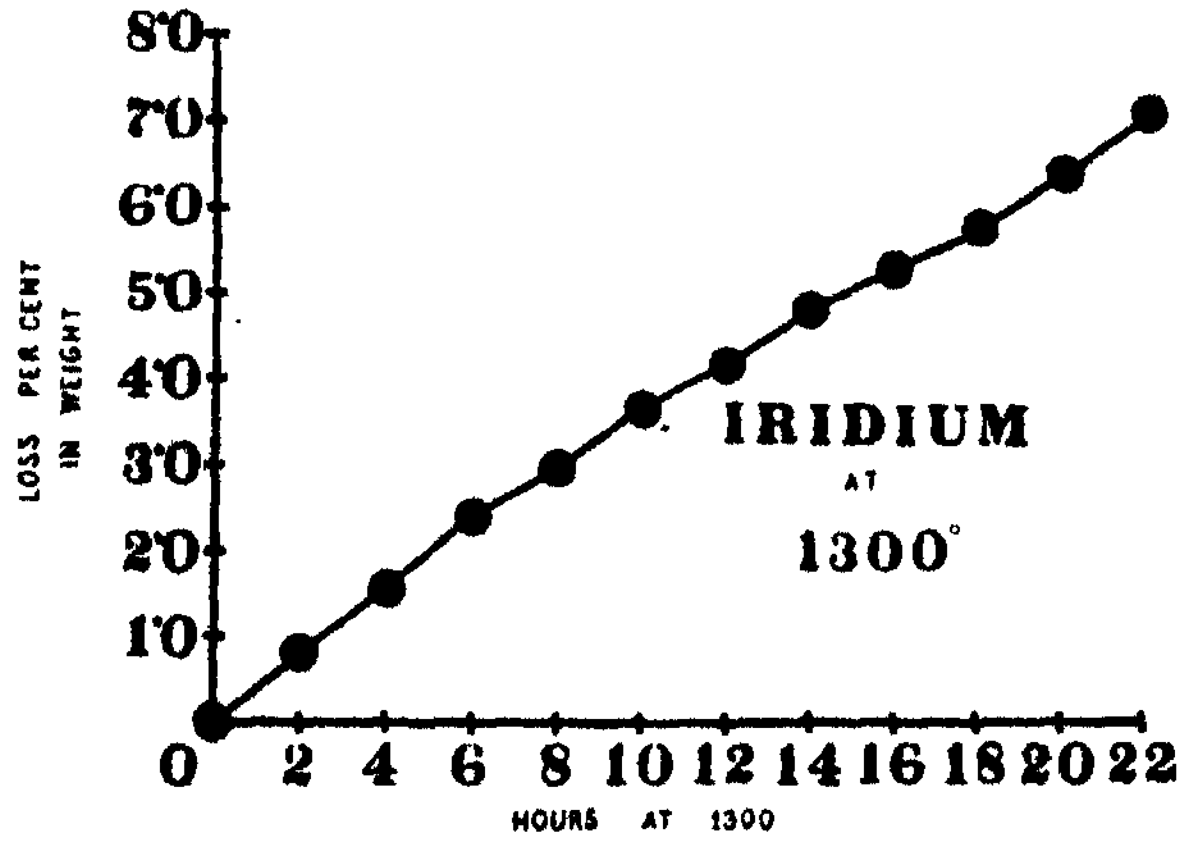

FIG. 5.

the temperature. After the last experiment at 1300° the crucible was exposed for two hours at a time to temperatures rising from 1000° to 1400°, with the following results :—

Table IV.

	Grains.	Loss.	
		Grains.	Per cent.
Weight of iridium at starting............	135·092	—	—
After 2 hours at 1000°....................	134·927	0·165	0·122
After 2 additional hours at 1100°	134·509	0·583	0·432
" " " 1200°	133·746	1·346	0·996
" " " 1275°	132·395	2·697	1·996
" " " 1320°	131·367	3·725	2·757
" " " 1400°	129·996	5·096	3·772

The curve, fig. 6, is plotted from the above data, and shows conclusively that the loss of weight for equal periods of time is proportional to the temperature.

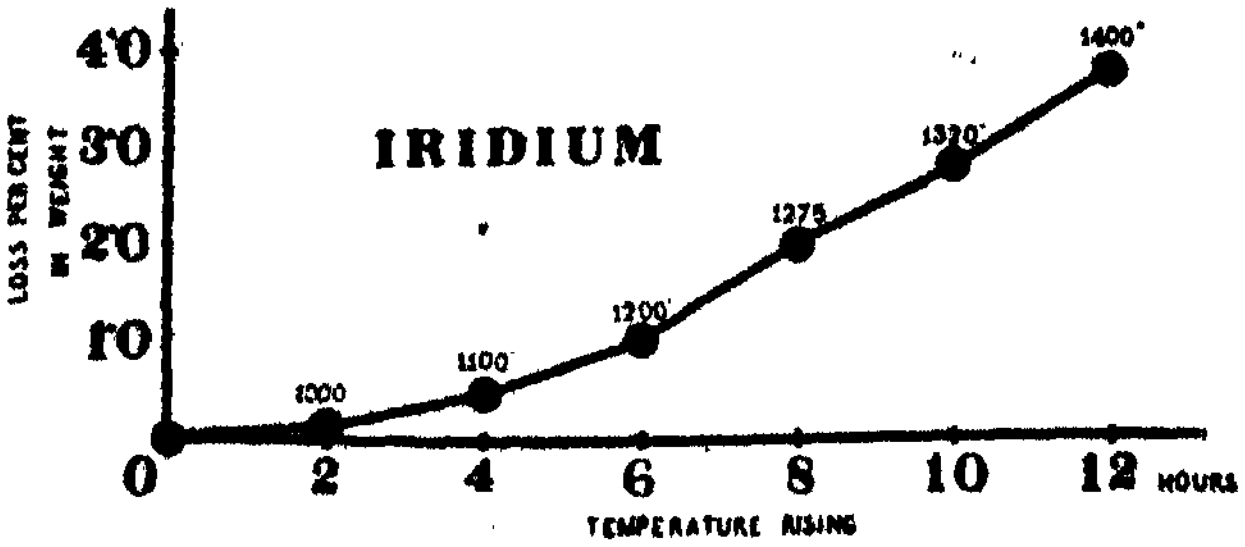

FIG. 6.

After this severe treatment the crucible, which had taken on a crystalline appearance over the whole surface when the series commenced, began to show approaching disintegration along its edges (fig. 7), and after several more heatings of two hours pieces began to crumble when touched with the forceps.

Fig. 7.

The disintegration of iridium has been examined by Messrs. Holborn and Austin,* who found that at high temperatures (1670°) a narrow strip disintegrated about ten times as rapidly in the air as platinum.

Rhodium at 1300°.

I next tried rhodium, a metal intermediate in fusibility between platinum and iridium, and similar to iridium in its resistance to chemical agents which attack platinum. In my paper above quoted† I suggested the use of rhodium for crucibles in the laboratory. Its low density (11 as against iridium 22) would be a great advantage in quantitative operations, as the weight of a rhodium crucible would be only half that of one made of platinum, and its cost would not be excessive.

The following table shows the losses in weight when metallic rhodium is exposed to a temperature of 1300° for two hours at a time for 30 hours in an electric furnace, the rhodium being cooled and weighed at intervals of two hours:—

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* 'Phil. Mag.,' Ser. 6, vol. 7, p. 388.

† 'Roy. Soc. Proc.,' A, vol. 80, p. 535.

Table V.

	Grains.	Loss.	
		Grains.	Per cent.
Original weight of rhodium	32·774	—	—
After 4 hours at 1300°, weighed	32·767	0·007	0·021
,, 6 ,, ,, ...	32·765	0·009	0·027
,, 8 ,, ,, ...	32·763	0·011	0·034
,, 10 ,, ,, ...	32·760	0·014	0·043
,, 12 ,, ,, ...	32·758	0·016	0·049
,, 14 ,, ,, ...	32·755	0·019	0·058
,, 16 ,, ,, ...	32·752	0·022	0·067
,, 18 ,, ,, ...	32·749	0·025	0·076
,, 20 ,, ,, ...	32·746	0·028	0·085
,, 22 ,, ,, ...	32·743	0·031	0·095
,, 24 ,, ,, ...	32·739	0·035	0·107
,, 28 ,, ,, ...	32·734	0·040	0·122
,, 30 ,, ,, ...	32·731	0·043	0·131

Fig. 8 shows the curve plotted from these data.

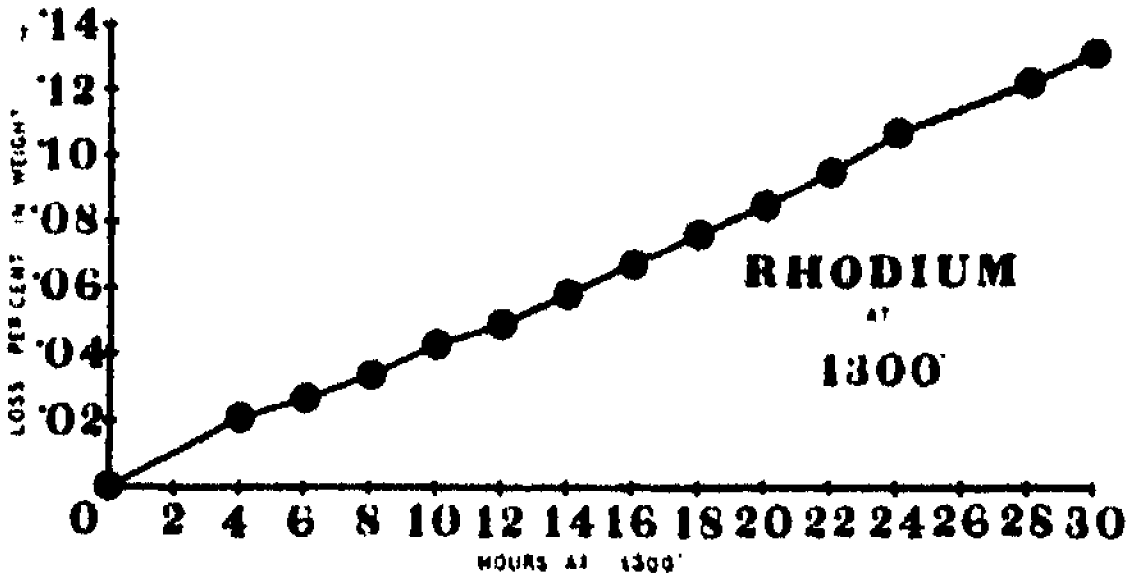

Fig. 8.

After the above heating the rhodium did not appear much changed. It was a little darker, as if with a slight tarnish, but showed no crystalline structure.

Ruthenium at 1300°.

Ruthenium does not lend itself to such experiments as the foregoing owing to the formation of a volatile oxide. A piece of the pure metal, in the form of a highly polished plate, exposed in the furnace to a temperature of 1300° for eight hours, lost 25 per cent. of its weight.

After this heating the ruthenium was of a dull black and was covered with a coating of oxide having a fused appearance.

The diagram (fig. 9) shows the loss per cent. in weight of the metals platinum, palladium, iridium, rhodium and ruthenium on the same scale when exposed to a temperature of 1300° for two-hourly periods.

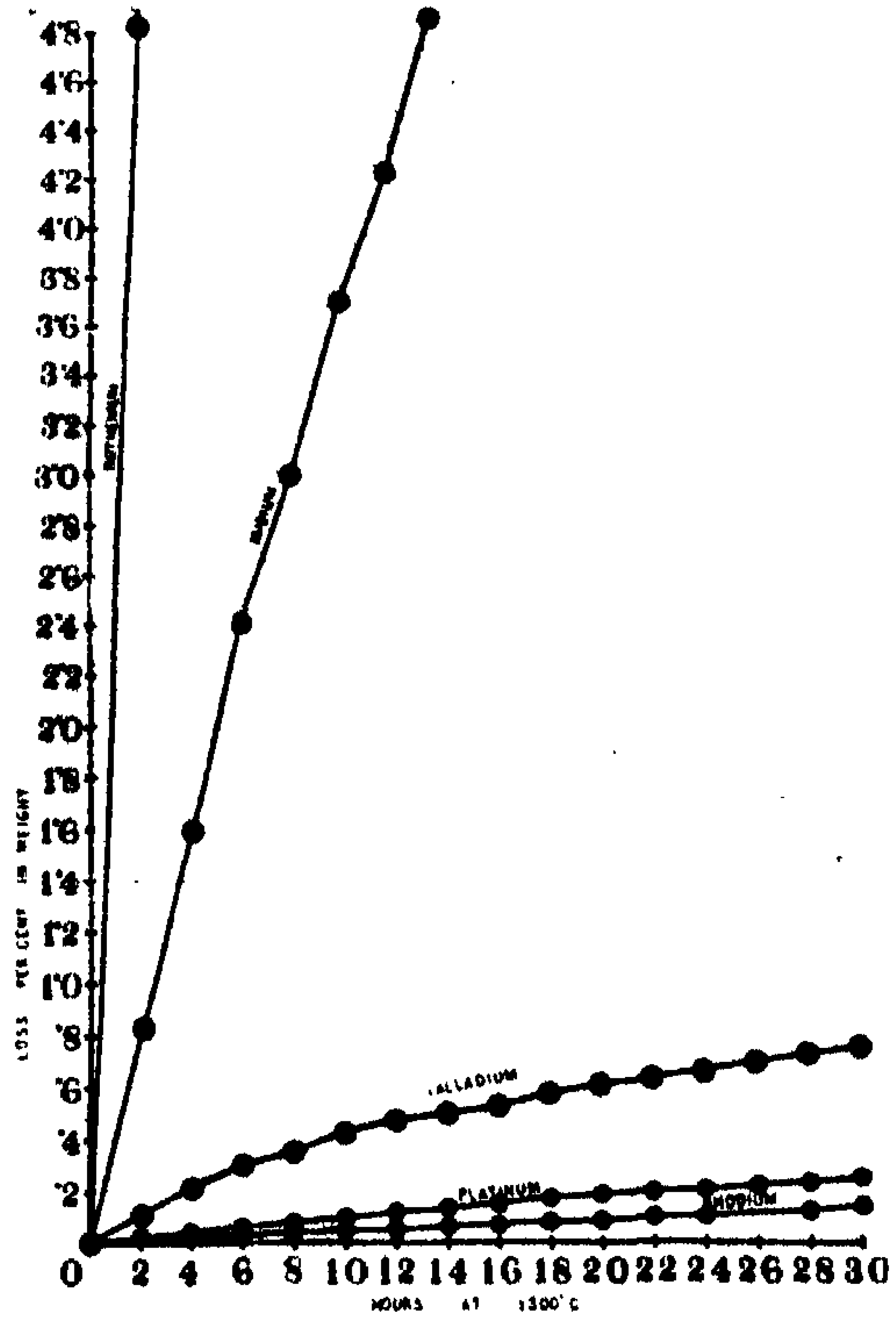

FIG. 9.

Having obtained such unexpected results at 1300° it was of interest to see how these metals would behave at a temperature sometimes employed in an analytical laboratory.

Platinum at 900°.

I therefore arranged a large Méker burner, with fused silica triangle and a surrounding clay cylinder to obstruct radiation, and with it heated an almost new platinum crucible. The thermo-couple showed a temperature of about 900° in the centre of the hot crucible. After being heated to this temperature for 10 minutes the crucible was cooled and transferred to the balance. It weighed 121·059 grains. It was now subjected to 10 successive heatings of two hours each to 900°, weighing each time. The original weight of 121·059 grains was not found to vary in the slightest degree, and the same experiment tried with other platinum crucibles gave a similar result. A temperature of 900° is a full orange heat, and, unless a blowpipe is used, is higher than platinum crucibles are usually subjected to in the laboratory.

Palladium at 900°.

Palladium was next tried at a temperature of 900° under the same conditions to which platinum was subjected. The following table shows the diminution in weight:—

Table VI.

	Grains.	Loss.	
		Grains.	Per cent.
Original weight of palladium	56·579	—	—
After 2 hours at 900°, weighed	56·570	0·009	0·0159
" 4 " "	56·560	0·019	0·0336
" 6 " "	56·550	0·029	0·0513
" 8 " "	56·585	0·044	0·0778
" 10 " "	56·527	0·052	0·0919
" 12 " "	56·521	0·058	0·1025
" 14 " "	56·512	0·067	0·1184
" 16 " "	56·505	0·074	0·1308
" 18 " "	56·500	0·079	0·1396
" 20 " "	56·491	0·088	0·1555
" 22 " "	56·487	0·092	0·1626
" 24 " "	56·481	0·098	0·1732
" 26 " "	56·478	0·101	0·1785
" 28 " "	56·477	0·102	0·1803
" 30 " "	56·476	0·103	0·1827

The palladium scarcely altered during these heatings. Beyond a faint pink tinge no signs of superficial oxidation could be detected, and the surface, with the exception of a few more blisters, presented practically the same appearance as it had after the 1300° series.

Iridium at 900°.

Having found platinum to be absolutely fixed at 900°, it was of interest to see how iridium would behave at that temperature. Another iridium crucible was taken, and its original weight, after good ignition, was found to be 175·374 grains. Heating to 900° over a Méker gas burner in air for 2 hours 25 minutes reduced the weight to 175·322. In Table VII is shown the gradual diminution in weight with the duration of heating.

After these successive heatings to 900°, the iridium crucible was a little darker than it was originally, but it had no crystalline moiré appearance, like the other one after having been heated for 22 hours to 1300°.

Table VII.

	Grains.	Loss.	
		Grains.	Per cent.
Original weight of iridium.............	175·374	—	—
After 2 h. 25 m. at 900°, weighed ...	175·322	0·052	0·030
" 4 h. 40 m. " " ...	175·297	0·077	0·044
" 6 h. 40 m. " " ...	175·289	0·085	0·048
" 8 h. 40 m. " " ...	175·268	0·106	0·060
" 11 h. 40 m. " " ...	175·244	0·130	0·074
" 14 h. " " ...	175·241	0·133	0·076
" 16 h. " " ...	175·221	0·153	0·087
" 18 h. " " ...	175·219	0·155	0·088
" 20 h. " " ...	175·215	0·159	0·091
" 22 h. " " ...	175·213	0·161	0·092

Rhodium at 900°.

Experiments were now instituted to see if a temperature of 900° continued for many hours would have any effect on metallic rhodium.

Table VIII.

Original weight of rhodium	32·731 grains.
After 2 hours at 900°, weighed	32·731 "
" 4 " "	32·732 "
" 6 " "	32·731 "
" 8 " "	32·731 "
" 10 " "	32·732 "

The weight remains almost exactly the same. The differences, amounting to 0·001 grain, equal to a difference of 0·003 per cent., are due probably to slight superficial oxidation to RhO, and reduction of the oxide to the metallic state in a reducing atmosphere.

I have plotted these curves on one diagram (fig. 10) so that the volatility of

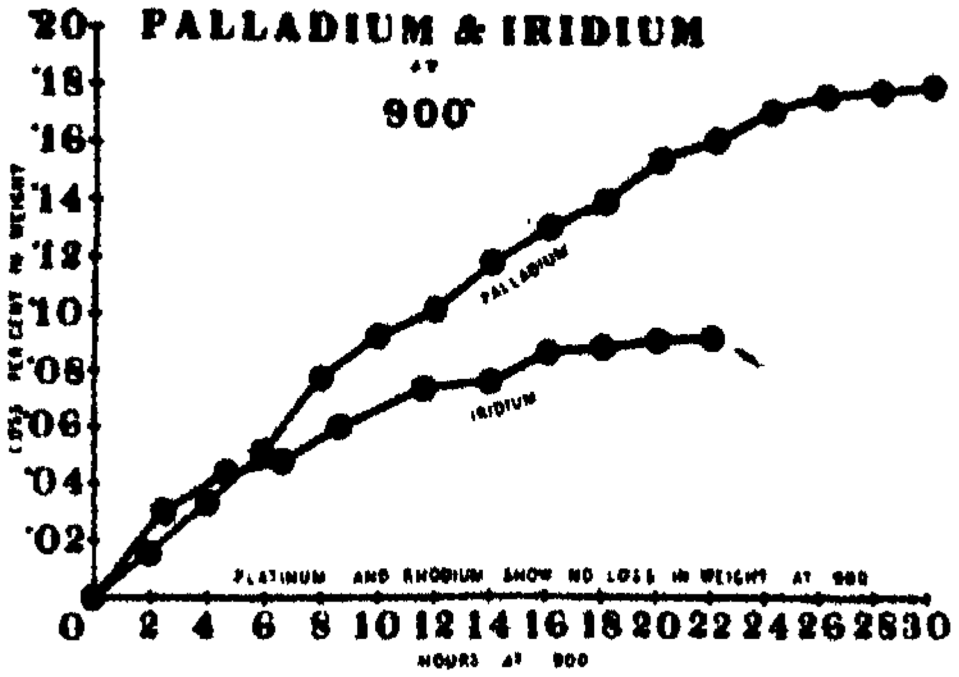

FIG. 10.

the metals at 900° can be compared one with the other, and also with the corresponding curve of metals at 1300°. The horizontal scale of hours is the same in each, but to render the curves at 900° distinct I have been obliged to make the vertical scale of percentage loss 10 times as large as it is in the 1300° curves.

Summary.

These results bear two explanations:—(1) The metal is volatile *per se* at these high temperatures, or (2) the metal unites with oxygen at a certain temperature, forming a volatile oxide, which may either volatilise unchanged, or may decompose at a higher temperature with deposition of the metal, the oxygen acting in this case as the temporary carrier of the metal. It is probable that each of these causes is active in one or other of the metals experimented with. I will take the case of the metal first tried, viz., platinum. The universal experience of chemists is against the supposition that platinum forms a volatile oxide below 1300°. Deville and Debray, who worked long and thoroughly on the platinum metals, agree that "platinum is distinguished from all the metals which accompany it in the mineral, by the fact that it does not unite direct with oxygen in whatever condition the two bodies are placed."*

The mode of occurrence of the beautiful crystals of platinum is against the supposition that they are a product of the decomposition of an oxide, for the crystals deposit on a part of the apparatus that is at a slightly lower temperature than the bulk of the metal, and it is inconceivable that platinum should unite with oxygen to form a volatile oxide at one definite temperature, and part with this oxygen and come down in metallic crystals at a little lower temperature.

The boiling-point of platinum is put by Kaye and Laby at about 2450°.† Moissan's electric furnace, in which the arc is used, is said by him to give with ease a temperature of 3500°, and here platinum enters into fusion in a few minutes, and soon volatilises. The metallic platinum collects in small brilliant globules and in powder on the cooler parts of the electrodes, or on the surface of the lower brick some centimetres from the crucible.‡ No mention is made of the metal condensing in crystals.

I must therefore come to the conclusion that platinum is absolutely non-volatile at 900°, a temperature easily attainable in an analytical laboratory, and that the formation of crystals of the metal in the electric furnace is a true case of sublimation.

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* 'Comptes Rendus,' 1878, vol. 87, p. 441.

† 'Physical Constants,' 1911, p. 49, Longmans.

‡ Moissan, 'Le Four Electrique,' p. 43.

The next metal, iridium, under experiment behaves differently to platinum. It is admitted that iridium is volatile at a high temperature. Thus, Mendenhall and Ingersoll[*] speak of melting iridium into a globule, and then re-melting it two or three times, before it entirely sublimed. This at a temperature above its melting-point, which these authors put at between 2300° and 2400°.

Waidner and Burgess,[†] describing an "iridium furnace," of which the essential part is an iridium tube 25 cm. long, 2 cm. in diameter, and 0·25 mm. wall thickness, state that, to avoid evaporation of the iridium, it was coated with Nernst's refractory earth mixture.

These illustrations, however, are taken from observations of experimentalists who were working with iridium at or near its melting-point.

At high temperatures below 1000° iridium oxidises, forming an oxide, Ir_2O_3, which is volatile. Deville and Debray consider the alleged volatility of the metal is due to the formation of this volatile oxide. They say: "Above 1000° all volatilisation becomes impossible in our atmosphere, because the oxide of iridium ceases to exist, and the metal is at least as fixed as platinum."[‡]

In my experiments the cold iridium was put into the furnace, previously heated to 1300° or thereabouts, and the metal quickly became hot. While it was rising to 1000° it oxidised superficially, and the oxide rapidly volatilised, accounting for the loss of weight.

I devised an experiment to see if iridium would volatilise at a high temperature in a vacuum. A fused silica tube, 1 cm. diameter and 20 cm. long, had a bulb 2½ cm. diameter blown on the end (fig. 11). In the bulb was put 27·619 grains of clean iridium, and the other end of the silica tube was drawn out for connecting with the pump and sealing. It was exhausted to a high vacuum and heated to near redness along its whole length, till all moisture and occluded gases had been removed; it was then sealed off.

The tube was placed bulb uppermost in the furnace in such a position that the iridium would be at the point of greatest heat, the lower part of the tube remaining comparatively cool. The bulb was kept at a temperature of 1300° for 30 hours. On examining the silica tube when cold, it was seen that the long-continued high temperature had caused the bulb and the upper part of the tube to devitrify, and become white and translucent, and that it had an irregular black deposit on the lower part, which, on examination, proved to be metallic iridium.

The iridium removed from the bulb was now found to weigh 27·600 grains, showing a total loss of 0·019 grain, or 0·069 per cent., in 30 hours.

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[*] 'Physical Review,' vol. 25, p. 13.

[†] 'Bulletin of the Bureau of Standards, Washington,' vol. 3, p. 163.

[‡] 'Comptes Rendus,' vol. 87, p. 445.

The presence of a deposit of iridium in the cooler end of the silica tube may thus be accounted for: during the heating of the bulb containing the iridium, a little air leaked in, and the oxide of iridium formed before the temperature became high enough to decompose it volatilised and deposited on the cooler part of the tube. There the oxide remained until the heat rose to the decomposing-point—somewhere about 1000°.

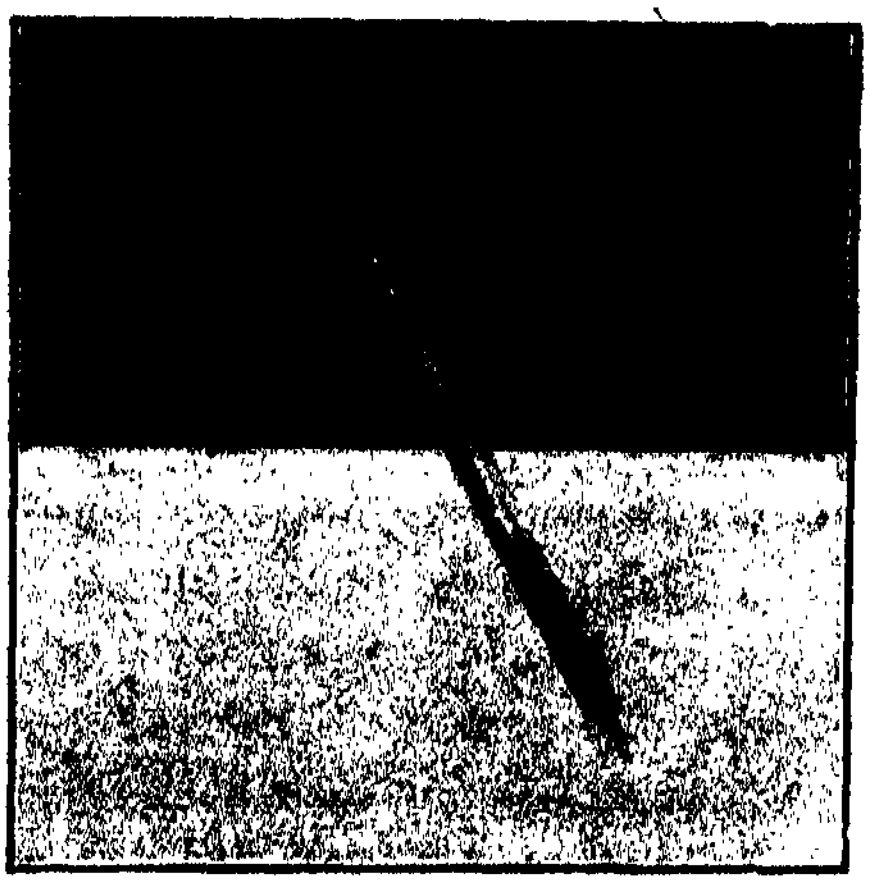

Fig. 11.

I must not conclude this paper without expressing my thanks to the firm of Johnson and Matthey, to whom I am indebted for many specimens of the pure metals used in this research.

On the Distribution of the Scattered Röntgen Radiation.

By J. A. CROWTHER, M.A., Fellow of St. John's College, Cambridge.

(Communicated by Prof. Sir J. J. Thomson. Received February 15,—Read March 21, 1912.)

Introduction.

The fact that a substance through which Röntgen rays from a focus tube are passing becomes itself a source of secondary Röntgen rays has long been known. The most probable explanation was given by Prof. Sir J. J. Thomson. If a Röntgen pulse is due to the acceleration of a charged electron, then if the electrons in the atom are free to move under the action of the electromagnetic forces in the wave front of the primary Röntgen pulse, their motion will be accelerated during the passage of the latter through the atom, and they will themselves become sources of secondary Röntgen radiation.

Considering only a single electron, the intensity of the secondary radiation at any angle α with the direction of motion will be proportional to $\sin^2\alpha$. If the primary beam is unpolarised, the motion of the electron may have any direction in the plane at right angles to the primary beam. The intensity of the scattered radiation in the direction θ with the primary beam is thus the mean of all the values of $\sin^2\alpha$ for that direction. It can easily be shown that this is proportional to $1+\cos^2\theta$. If I'_θ is the intensity of the scattered radiation in the direction θ, we thus have

$$I'_\theta = I'_{\pi/2}(1+\cos^2\theta). \tag{1}$$

This expression gives a distribution symmetrical about the primary beam and about a plane through the radiator at right angles to the primary beam. There is a minimum of radiation in this plane, and a maximum, equal to twice the minimum, at right angles to this plane, both in the forward and backward direction. Prof. C. G. Barkla some time ago found that the radiation coming back from a radiator in directions close to the primary beam was nearly twice as great as that in a direction at right angles to it, and thus obtained evidence in favour of the theory.

In the course of some experiments on the energy of the scattered Röntgen radiation,* it was found necessary to know the actual distribution of the radiation round the radiator, and experiments were made to determine it. A narrow pencil of Röntgen rays was allowed to fall on a suitable radiator, mounted on the axis of a large wheel carrying an ionisation chamber. By turning the wheel, the latter could be placed at different angles with the radiator, and the intensity of the scattered radiation measured at different angles with the primary beam.

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* J. A. Crowther, 'Proc. Camb. Phil. Soc.,' November, 1910; 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 29.

It was found that the theoretical expression did not exactly represent the experimental results. The distribution of the radiation which came back from the radiator agreed closely with that predicted by the theory, but, at any given angle with the primary beam, there was always more radiation scattered in the forward direction than in the backward. This dissymmetry between the two sides of the radiator increased as the direction of the primary beam was more nearly approached. Thus for an aluminium radiator there was, at an angle of 30° with the primary beam, nearly three times as much scattered radiation in the forward as in the reverse direction. The actual distribution in this case is shown in fig. 1. The value of the intensity of the scattered radiation in any direction θ is represented by the length of the vector drawn in that direction from the centre R. The full curve shows the distribution actually observed. The inner broken curve represents the theoretical distribution. For the return radiation, the two curves are practically coincident.

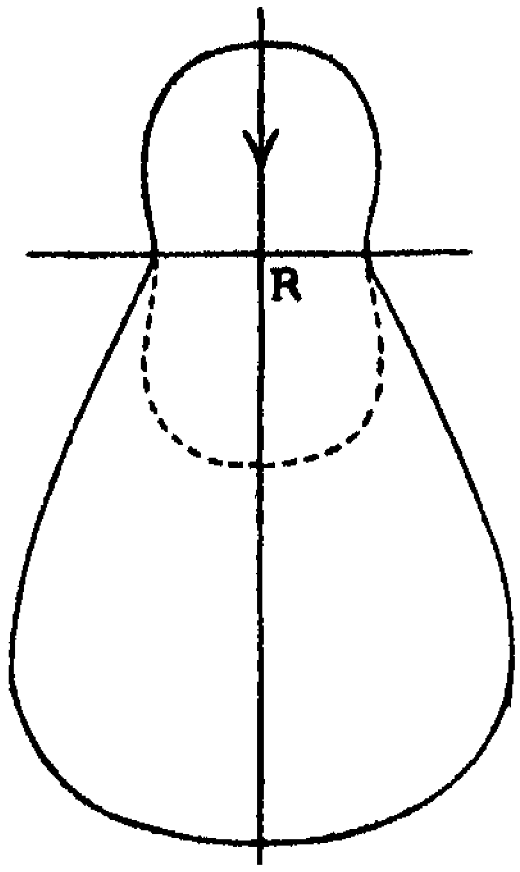

FIG. 1.

Somewhat later Prof. C. G. Barkla[*] published an account of a similar series of experiments. He only observed dissymmetry at angles of less than 30° with the primary beam, but Owen,[†] who repeated my experiments in the Cavendish Laboratory, confirmed the results I had obtained. He also found that the dissymmetry decreased as the primary rays became harder. We shall return to this result later.

The fact that the distribution of the return radiation agreed so closely with that predicted by the theory of scattering naturally suggested that the excess of secondary radiation on the forward side of the radiator might be due to some other cause of secondary radiation. Experiments made on the absorption of the scattered radiation in the forward and backward directions failed to reveal any appreciable difference in the character of the rays in the two directions. The coefficient of absorption was in each case very nearly the same as that of the primary beam.

It was suggested that a possible source of this excess radiation might be found in a diffusion or irregular refraction of the primary beam itself by the substance of the radiator. Let us suppose that a primary Röntgen pulse is deflected in passing through the field of an atom by some small angle α. The direction of this deflection will be perfectly arbitrary, and, the atoms being sufficiently numerous, we can compound these deflections by means of the theorem, due to Lord Rayleigh, on the composition of random displacements. It can be shown that the probability of a displacement between the angles θ and $\theta + \delta\theta$ is

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[*] C. G. Barkla and T. Ayres, 'Phil. Mag.,' 1911, vol. 21, p. 270.

[†] E. A. Owen, 'Proc. Camb. Phil. Soc.,' 1911, vol. 16, p. 161.

$$\frac{2}{n\alpha^2} e^{-\theta^2/n\alpha^2} \theta \delta\theta, \tag{2}$$

where n is the number of atoms traversed by the pulse in its passage through the radiator.

The probability of a deflection greater than θ is equal to $e^{-\theta^2/n\alpha^2}$. If we now assume that the difference between the symmetrical distribution which we should expect on the theory of scattering explained above and the actual experimental curve is due to some effect of this nature, we can, by measuring the total amount of this excess radiation beyond a certain angle θ, obtain a value for this quantity. Knowing θ, we can then calculate the value which the constant $n\alpha^2$ must have in order to explain our results.

With the aid of this constant we can calculate the value which this excess radiation should have across a small area placed at any angle with the primary beam. If the area remains constant this value should increase rapidly as the primary beam is approached. Experiments made at small angles with the primary beam should therefore enable us to test the accuracy of our assumptions.

In order to measure the intensity at small angles with the primary beam, an ionisation chamber closed with a lead shutter having a narrow slit in it was employed.* By means of a micrometer screw the slit could be accurately set at any desired small angle with the axis of the primary beam. From the value of $n\alpha^2$ previously obtained the intensity of radiation to be expected across the slit in any given position could be calculated. On making the experiment it was found that the intensity of the radiation at an angle of about 2° with the primary beam was not more than 2 per cent. of the intensity to be expected, if the primary beam was suffering irregular refraction.

We must conclude, therefore that the dissymmetry observed is not due to a refraction of the beam as a whole, a conclusion which is also supported by the experiments to be described. The experiments would not preclude the possibility of the dissymmetry in the scattered radiation being due to irregular refractions if we could assume that only a small fraction of the primary Röntgen rays were thus affected. Only a small fraction of the encounters between the Röntgen rays and the atoms result in ionisation. If we suppose that in a similar way only a small fraction of the collisions result in any appreciable deflection of the primary ray it might be possible to explain the results obtained. I am indebted for this suggestion to Prof. Sir J. J. Thomson, to whom I wish to express my best thanks.

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* J. A. Crowther, 'Proc. Camb. Phil. Soc.,' 1911, vol. 16, p. 177.

Let us assume, however, for the present that the excess of the forward over the returned scattered radiation is due to some effect other than the symmetrical scattering of the primary beam. It seemed desirable that further and more accurate experiments should be made to determine its exact distribution and its variation with the hardness of the primary rays.

Experimental Details.

A brief description of the apparatus may be desirable, as it differs in some respects from that described in the previous papers.

The radiator R (fig. 2) is carried on an aluminium frame, the different parts of the framework being well out of the path of the primary rays. The framework, which carried a pointer moving over a circular scale, could rotate about the axis, and the radiator could thus be set at any desired angle with the primary beam.

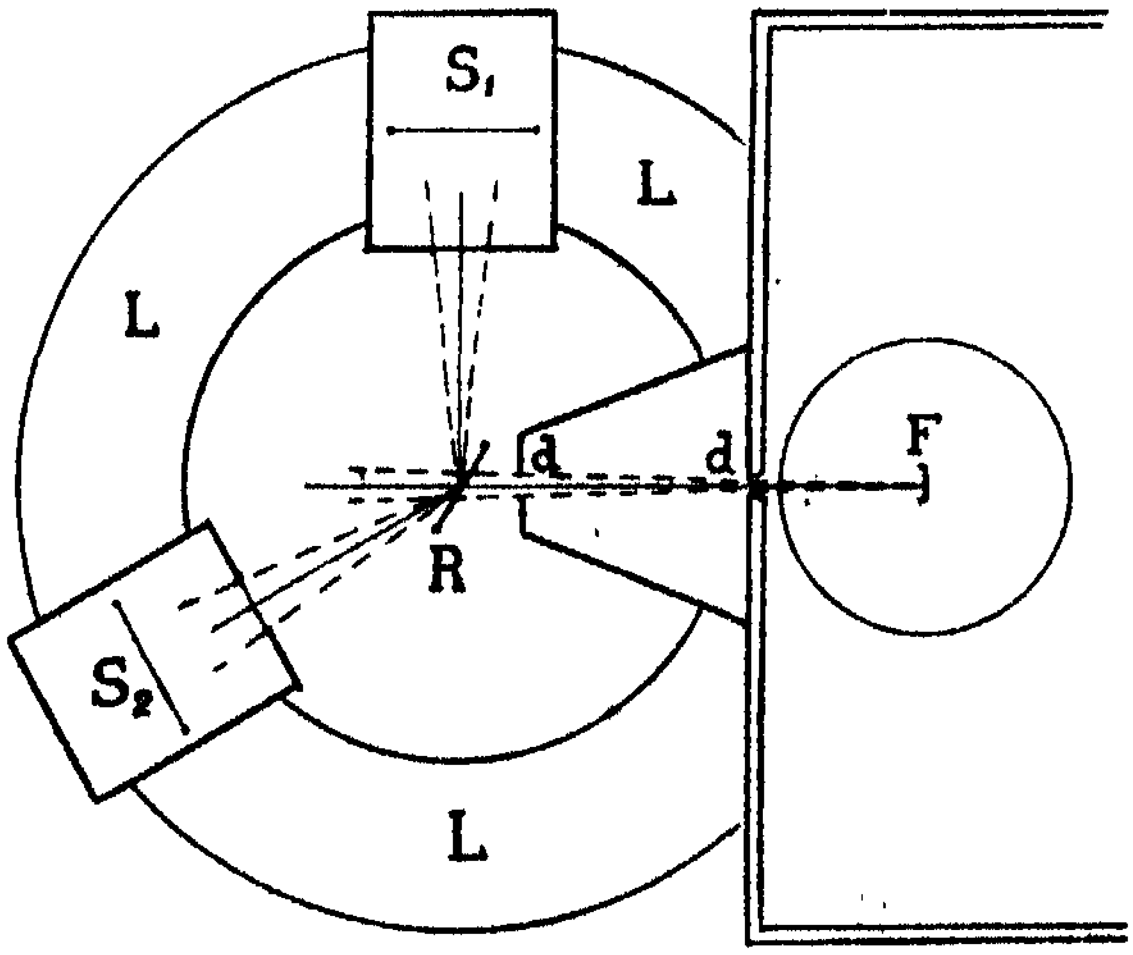

Fig. 2.

The primary beam from the focus tube F was confined to a narrow rectangular pencil, by means of the lead diaphragms *d*, *d*, rectangular in shape. It was found experimentally that there was very little radiation outside the geometrical cross-section of the beam as so defined.

Two equal and similar ionisation chambers S_1, S_2, were fitted up with aluminium leaf electrodes as described in the previous papers. They were mounted on carriers running on a circular geometrical slide L, L, the centre of which was immediately beneath the axis of the radiator. Each of the chambers was connected to a separate tilted electroscope in the way previously described, so that it could be moved freely round the circular slide without disturbing the connections.

Each ionisation chamber had an aperture of 2·60 cm. in width, and was placed 15 cm. from the centre of the radiator R. The angle subtended at the radiator by the aperture was therefore about 10°. The ratio of the ionisation currents in the two chambers for equal intensities of radiation entering them was determined experimentally by placing them at equal angles with the primary beam, and on opposite sides of it. The ratio was found to be constant for all angles. The distribution of the scattered radiation is thus symmetrical on each side of the primary beam.

In performing the experiments, one of the two chambers, say S_1, was placed at an angle of 90° with the direction of the primary beam. The other chamber was moved round to the angle at which it was desired to measure the intensity of the scattered radiation. The radiator was then turned so that its normal bisected the angle between the secondary beams entering the two chambers, that is to say the angle S_2RS_1 in the figure. It can easily be seen that in this position the lengths of path in the radiator of the two secondary beams are the same. The two beams therefore undergo the same relative absorption, and no further account need be taken of this factor. This adds considerably to the convenience and accuracy of the experiment, as it is difficult to keep the hardness of the focus tube quite constant over a series of experiments.

Let I_θ be the intensity of the scattered radiation entering the ionisation chamber when its axis is inclined at an angle θ with the primary beam. The ratio of the two ionisation currents (corrected for the small difference between the two chambers when subject to the same intensity of radiation, as explained above) gives the value of the ratio of $I_\theta/I_{\pi/2}$. Since the areas of the apertures of the two chambers are the same, this ratio is also a measure of the intensity of the secondary radiation per unit area in the two directions.

There is a certain amount of ionisation in the two chambers in the absence of the radiator; this can be measured separately, and allowed for. It is principally due to the scattered Röntgen radiation from the air traversed by the primary beam, and is only very appreciable at very small angles with the primary rays.

The first experiments were made with a radiator of aluminium foil. Subsequently, radiators made by soaking best Swedish filter paper in paraffin wax were employed. These have a much smaller coefficient of absorption for the rays than the aluminium, and it is possible, therefore, to obtain far more secondary radiation from them than from aluminium. They were therefore principally employed in the investigations which follow.

Experimental Results.

In Table I are given the results obtained with a radiator of filter paper 0·35 cm. in thickness. The first column gives the direction θ with the primary beam at which the intensity I_θ was measured. The succeeding columns give the value of the ratio $I_\theta/I_{\pi/2}$ at those angles for primary rays of different hardness. The hardness of the primary beam is fixed by the length of the spark-gap (measured between two brass spheres) which is just sufficient to extinguish the focus tube when connected across its terminals. The length of this spark-gap in centimetres stands at the head of the column to which it refers in the table.

Table I.—Values of $I_\theta/I_{\pi/2}$ for Filter-paper Radiator.

θ.	1·0.	1·2.	2·1.	3·5.	4·0.	Theoretical distribution.
°						
10	3·60	3·45	4·24	4·30	4·60	1·97
15	3·25	3·70	3·58	3·25	2·86	1·92
20	2·90	3·00	2·75	2·73	2·30	1·88
25	2·51	—	2·28	2·34	1·97.	1·81
30	2·14	2·13	1·98	2·09	—	1·75
40	1·78	1·73	1·66	1·67	1·52	1·59

The last column of the table gives the value of the ratio of the intensity per unit area of the scattered radiation in the direction θ to that at right angles to the primary beam, deduced from equation (1), p. 478. For brevity, we shall refer to this as the theoretical value. It is, of course, independent of the hardness of the primary rays.

Table II gives the results of experiments made with filter-paper radiators of different thicknesses. In these experiments the two ionisation chambers were fixed at angles of 25° and 90° respectively, and the hardness of the bulb was kept as constant as possible, with an equivalent spark-gap of about 1·5 cm. The first column gives the thickness of the radiator in centimetres, the second the corresponding values of the ratio of I_θ to $I_{\pi/2}$. It will be seen that, within the limits of the experimental error, the ratio is independent of the thickness of the radiator. I have shown in a previous paper* that the intensity of the radiation scattered at an angle of 90° with the primary beam is simply proportional to the thickness of the radiator. It follows, therefore, that the intensity of the radiation at an angle of 25° with the primary beam, and therefore also the intensity of what we have called the excess radiation, is also proportional to the thickness of the radiator.

Table II.—Variation in the Ratio $I_\theta/I_{\pi/2}$ for Filter-paper Radiators of Different Thickness. Equivalent Spark Gap = 1·5 cm.

Thickness of radiator.	$I_{25°}/I_{\pi/2}$.
cm.	
0·20	2·36
0·26	2·30
0·36	2·38
0·42	2·34
0·69	2·28
0·84	2·40

Table IV.—Aluminium Radiator. Spark Gap = 1·2 cm. b = 0·44.

θ.	E_θ.	M_θ.	E_θ/M_θ.
°			
15	2·0	1·04	1·92
30	2·6	1·28	2·03
45	1·6	0·86	1·87
60	0·7	0·37	1·89
75	0·2	0·09	2·2

Reduction of Results.

The figures in Table I give directly the intensity of the scattered Röntgen radiation across an aperture of fixed area, placed so that the line joining its centre to the radiator makes an angle θ with the direction of the primary beam. If the primary rays are unpolarised, the intensity of the scattered radiation at an angle θ with the primary beam is independent of the plane in which it is measured. The rays from most focus tubes show a certain amount of polarisation; for the bulb used in these experiments it amounted to about 8 per cent. In order to reduce the effect as far as possible, the focus tube was placed so that the stream of cathode rays in it was at right angles to the plane in which the measurements were made. In this position the effect of the admixed polarised rays would be to add to both numerator and denominator of the ratio I_θ to $I_{\pi/2}$ a small constant fraction depending on the quantity of polarised radiation present, and thus to reduce slightly the theoretical value. The maximum correction for the bulb used did not amount to more than 4 per cent.

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* J. A. Crowther, 'Proc. Camb. Phil. Soc.,' 1911, vol. 16, p. 365.

Allowing, therefore, when necessary for the polarisation, we can now proceed to calculate from our results the whole intensity of the Röntgen radiation scattered by the radiator at an angle θ with the primary beam.

Let $R_\theta \delta\theta$ be the energy of the scattered Röntgen radiation included within a hollow cone of angle θ and increment $\delta\theta$. We will call R_θ the whole intensity of the radiation in the direction θ. The area swept out by this hollow cone on a sphere of radius r passing through the windows of the two ionisation chambers is $2\pi r^2 \sin\theta\,\delta\theta$.

Now if α is the area of the window of the ionisation chamber, supposed small enough to be included in this belt, the intensity I_θ of the rays entering the ionisation chamber is equal to

$$R_\theta \delta\theta \frac{\alpha}{2\pi r^2 \sin\theta\,\delta\theta}.$$

But α, the area of the window, is constant, and r is constant. We may write, therefore, $R_\theta = (\text{constant}) \times I_\theta \sin\theta$. To obtain R_θ from the readings in Table I, we must multiply by the corresponding values of $\sin\theta$.

In the same way if we denote by $S_\theta \delta\theta$ the whole of the true scattered radiation (*i.e.* the radiation scattered in accordance with the theory) included in the hollow cone of angle θ and increment $\delta\theta$, we have $S_\theta = (\text{constant}) \times I'_\theta \sin\theta$, where I'_θ is the intensity of this radiation entering the ionisation chamber in the direction θ. In order to find S_θ, therefore, we have to multiply the values given in the last column of Table I by the corresponding value of $\sin\theta$.

The difference between the values of $R_\theta \delta\theta$ and $S_\theta \delta\theta$ for any given angle θ gives the amount of the secondary radiation which has still to be explained. Let us denote the intensity of this excess radiation in the direction θ by E_θ. Then

$$E_\theta \delta\theta = (R_\theta - S_\theta)\,\delta\theta.$$

The various stages of the calculation for the case of a radiator of filter paper of thickness 0·36 cm. and for an equivalent spark-gap of 2·1 cm. are given in Table III.

The first column of this table gives the angle θ at which the measurements of I_θ were made. The second column gives the corresponding value of I_θ in terms of $I_{\pi/2}$, the radiation at right angles to the primary beam, taken from Table I. The third column contains the values of $I_\theta \sin\theta$. As we have shown above this is proportional to R_θ. The fourth column gives the corresponding value of S_θ deduced from (1). The difference between them, given in the fifth column of the table, gives the magnitude of the effect which remains to be explained. In other words, assuming that the distribution of the scattered radiation is that given by (1), p. 478, the fifth column of Table III gives the distribution of the secondary radiation whose origin is still to be explained.

Table III.—Filter-paper Radiator. Equivalent Spark Gap 2·1 cm.

θ.	I_θ.	$I_\theta \sin\theta$.	Theory.	E_θ.	M_θ.	E_θ/M_θ.
°						
0	—	0·00	0·00	**0·00**	—	—
10	4·24	0·74	0·34	**0·40**	2·52	0·159
15	3·58	0·93	0·50	**0·43**	2·60	0·165
20	2·75	0·94	0·64	**0·30**	2·10	0·143
25	2·28	0·96	0·76	**0·20**	1·36	0·147
30	1·98	0·99	0·88	**0·11**	0·72	0·158
40	1·66	1·06	1·02	**0·04**	0·12	(0·33)
I	II	III	IV	V	VI	VII

I. Angle of measurement of scattered radiation.
II. Values of $I_\theta/I_{\pi/2}$.
III. $I_\theta/I_{\pi/2}$ multiplied by $\sin\theta$ to obtain the whole radiation between θ and $\theta + \delta\theta$.
IV. Value of same quantity on simple theory of scattering.
V. Difference between Columns III and IV, giving excess radiation.
VI. Value of $M_\theta = 2/b \,.\, e^{-\theta^2/b}\,\theta$, where $b = 0{\cdot}103$.
VII. Ratio of Columns V and VI.

These operations are represented graphically in fig. 3. The lower unbroken curve gives the relation between S_θ, the intensity of the scattered radiation on the theory of scattering, and θ. The upper unbroken curve represents the experimental curve for the measured radiation R_θ. The difference between the ordinates of these two curves is therefore the value of the excess radiation E_θ for the angle at which the ordinates are drawn. This difference is represented on three times the vertical scale of the other curves, by the broken curve in the figure. This broken curve therefore represents the distribution of the excess radiation. It will be seen that it rises rapidly at first to a sharp maximum at an angle of about 13° with the direction of the primary beam, and then falls, at first rapidly and then more slowly, to a value which approaches zero as θ approaches 90°.

We have, of course, tacitly assumed, in making our calculations, that the intensity of the excess radiation is inappreciable at angles of 90° and more with the primary beam. That this is practically the case is shown by the fact that all the experiments have proved that the distribution of the scattered radiation at angles of 90° and above is very closely in agreement with the distribution calculated from equation (1).

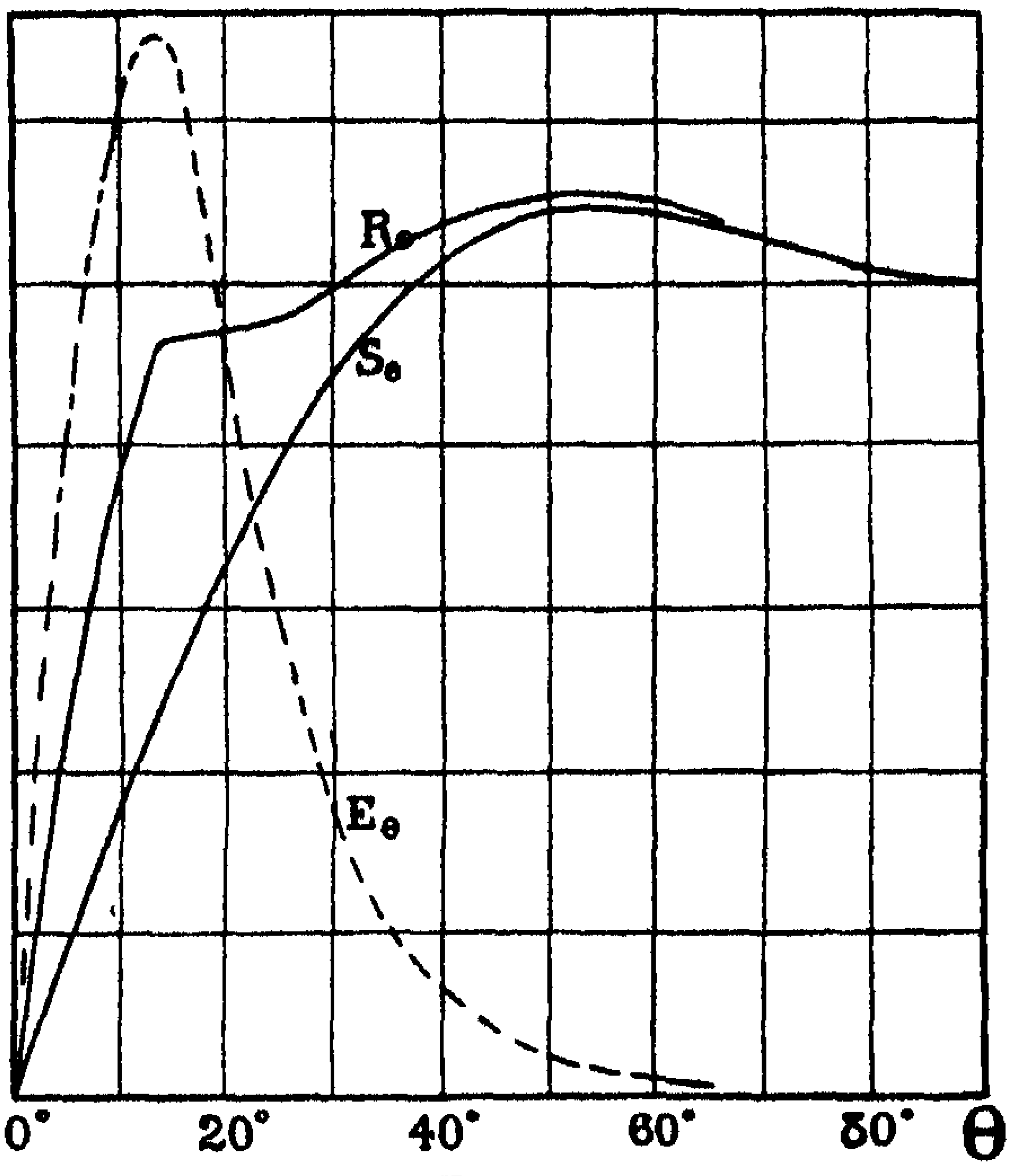

FIG. 3.

Exactly similar curves can be drawn for rays of other degrees of hardness. The curves given in fig. 4 represent the distribution of the excess radiation for some of the experiments given in Table I. It will be seen that they

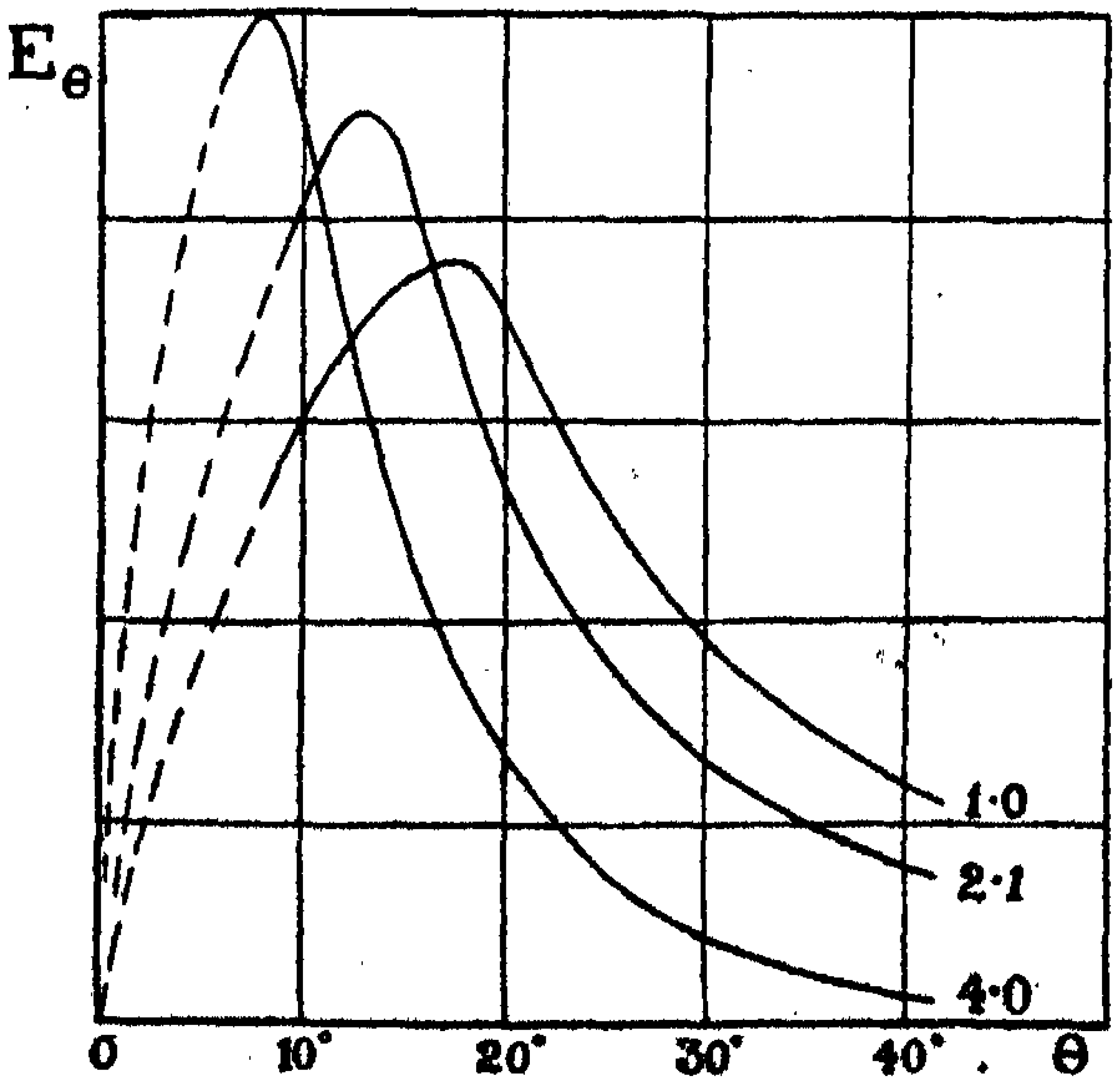

FIG. 4.

are all very similar in shape. As the rays get harder, however, two changes occur: (1) the whole area of the curve gets less, that is to say the total amount of the excess radiation decreases, and (2) the maximum of the curve gets nearer and nearer to the primary beam.

These curves enable us to explain the results obtained by Owen for hard rays. With his apparatus, he was unable to make experiments at angles less than 30° with the primary beam. Drawing an ordinate at $\theta = 30°$ it will be seen that the height of the ordinate, which measures the excess radiation over the theoretical value and therefore the dissymmetry in the position $\theta = 30°$, rapidly diminishes as the hardness of the rays increases. For rays of an equivalent spark-gap of 4 cm. it is already almost inappreciable, and thus, for primary rays of this hardness, the distribution of the radiation at angles greater than 30° would be that of the simple scattered radiation. There would be no appreciable dissymmetry. The more complete curve given in fig. 4 shows that there is, even for rays of this hardness, a considerable amount of excess radiation, but the maximum is close to the primary beam.

The actual dissymmetry observed at any angle θ therefore depends upon two factors:—

(*a*) The whole area of the curve, and

(*b*) The position of the maximum of the curve.

Measurements made at an angle of 10° or less would show an actual increase in the dissymmetry as the hardness of the rays increased.

Distribution of the Excess Radiation.

We must now proceed to consider the shape of these distribution curves more closely. It may be noted in passing that as these curves represent the difference of two curves their accuracy diminishes very rapidly when this difference becomes small compared with either of the curves. Owing to the small amount of scattered radiation entering the ionisation chambers under the conditions of the experiment, and the difficulty of keeping the conditions quite constant during the experiments, it would be futile to expect an accuracy of more than about 2 per cent. or 3 per cent. in the measurements of the intensity of radiation. An error of this amount in the measurement at an angle of 40° would introduce an error of as much as 20 per cent. in the difference we are measuring. We shall therefore confine our attention to angles of less than 40°, where the difference to be measured is relatively greater and the proportionate error correspondingly less.

Considering the curves of fig. 4 in detail, one may note their general resemblance to the curves representing the distribution of a parallel pencil of

β-rays after passing through a thin sheet of matter. The author has shown that this case may be represented closely by the expressions given on p. 480, based on the theorem of Lord Rayleigh on random displacements. If the present curves are to be of this form, the intensity E_θ of the excess radiation must be expressible in the form

$$E_\theta \delta\theta = 2K/b.e^{-\theta^2/b}\theta\delta\theta, \tag{3}$$

where b has been written for $n\alpha^2$, and K is a constant. It is evident that K is the ratio of the whole of the excess radiation round the radiator to the intensity, $I_{\pi/2}$, of the scattered radiation entering the ionisation chamber at right angles to the primary beam. Writing M_θ for the expression $2/b.e^{-\theta^2/b}\theta$ we see that if (3) expresses the actual experimental distribution of the excess radiation we must have $E_\theta/M_\theta = K$, a constant for all values of θ.

In order to determine the value of b for a given experimental curve it is most convenient to consider the position of the maximum. Differentiating with respect to θ and equating to zero, we have

$$1-2\theta^2/b = 0, \quad \text{so that} \quad b = 2\theta^2. \tag{4}$$

The value of θ for which the excess radiation reaches a maximum can be found from the experimental curves. Taking the case represented in fig. 3 this maximum occurs at an angle of 13° or 0·227 radian; the corresponding value of b is, therefore, 0·103. Substituting in the formula we obtain the values of M_θ given in Column 6 of Table III. The last column of this table contains the values of E_θ/M_θ, or K. We have shown that if our experimental curves are expressible by equation (3) this ratio must be constant. Similarly if this ratio is constant we may assume that the distribution of the excess radiation is represented by this expression. The last column of Table III shows how nearly this is the case.

The agreement is, on the whole, satisfactory. There is no systematic variation from the mean value as θ increases, and the fluctuations from the mean are not greater than might have been reasonably expected from the nature of the experiments. The calculations from the other sets of observations showed a similar agreement.

Similar experiments and calculations were also made for an aluminium radiator. The results are given in Table IV. The angle of maximum radiation is much greater than for the filter-paper radiators, and the whole area of the curve is much larger. The agreement between the experimental and theoretical curves is, however, equally satisfactory.

We may conclude then that the distribution curves for the excess radiation have the form we have suggested for them, and that the intensity of the excess radiation at an angle θ can be represented by equation (3).

Constants of the Curves.

The values of the various constants of this expression depend upon (1) the nature of the radiator, and (2) the hardness of the exciting rays. So far as they have been determined they are given in Table V.

Table V.

Equivalent spark-gap.	$\theta_{\max}$.	b.	K.	E/S.	f.
			Filter paper.		
cm.	°				
1·0	18	0·204	0·184	0·0120	0·0032
1·2	16	0·157	0·176	0·0114	0·0031
2·1	13	0·103	0·160	0·0097	0·0026
3·5	10	0·061	0·12	0·0078	0·0021
4·0	8	0·039	0·110	0·0071	0·0019
			Aluminium.		
1·2	27	0·44	1·90	0·124	0·036
I	II	III	IV	V	VI

I. Equivalent spark gap of focus tube.
II. $\theta_{\max}$, the angle at which E_θ reaches its maximum value.
III. Corresponding value of constant b ($b = 2\theta^2$).
IV. Corresponding value of constant K.
V. Ratio of whole excess radiation to whole scattered radiation.
VI. Coefficient of excess radiation (see p. 491).

The first part of the table deals with the radiators of waxed filter paper; the last row refers to a radiator of aluminium. The first column of the table gives the equivalent spark-gap of the focus tube with which the experiments were made. The second gives the angle at which the excess radiation reached its maximum value, and the third the corresponding value of the constant b. It will be seen that, as the spark-gap increased, the maximum of the excess radiation moved in towards the direction of the primary beam, and the value of b in consequence diminished. Comparing the results for filter paper and aluminium it will be seen that the maximum occurs much further out for aluminium than for filter paper. Taking the case of incident rays of equal hardness, it may be noticed that the ratio of the values of b for aluminium and filter paper is 0·44/0·157 or 2·8. This is very nearly the ratio of the densities of the two radiators (2·7 : 1).

The value of K, which is proportional to the whole energy of the excess radiation, is given in the fourth column of Table V. It will be seen that it decreases as the primary rays get harder. It will be noticed also that the value for aluminium is more than ten times that for the filter paper. Experiments with other radiators of higher atomic weight are very desirable. Owing to their high coefficients of absorption, and to the presence of fluorescent radiation in such large amounts as to mask almost completely the radiation we wish to measure, it is difficult to make the measurements required with any degree of accuracy. Our experiments show that the excess radiation is not proportional to the density, the emission per unit mass being four times as great for aluminium as for filter paper.

Relative Intensities of the Radiations.

The secondary Röntgen radiation round a radiator (in the absence of the homogeneous secondary radiation which is distributed, as we have previously shown, uniformly round the radiator) can thus be represented as the sum of two radiations, the scattered radiation distributed in accordance with (1), p. 478, and the excess radiation given by equation (3). We can calculate from our results the intensities of these two radiations relative to each other and to the primary beam.

Let E and S be the whole intensities of the excess and scattered radiations respectively given out by the radiator. From p. 489 we have $K = E/I_{\pi/2}$. We have seen that we may regard the intensity $I_{\pi/2}$ as being due almost entirely to the true scattered radiation. Calling 2δ the angle subtended at the centre of the radiator by the window of the ionisation chamber (0·172 radian in these experiments) we have

$$_{\pi/2}/S = \int_{\frac{1}{2}\pi-\delta}^{\frac{1}{2}\pi+\delta} S_\theta d\theta \bigg/ \int_0^\pi S_\theta \, d\theta = 0{\cdot}065$$

on evaluating the integrals.

Thus $$E = KI_{\pi/2} = 0{\cdot}065\ KS.$$

The values of K are given in the fourth column of Table V, the corresponding values of E/S in the fifth column of the same table. For filter paper the energy of the excess radiation is only a small fraction of that of the scattered radiation. It is much more important in the case of aluminium. The ratio decreases as the primary rays become harder.

Energy of the Scattered Radiation.

In order to calculate this it is necessary to know the ionisation produced by the primary beam falling upon the radiator in terms of the intensity $I_{\pi/2}$ entering the standard chamber. This can be done directly by turning the chamber S_2 until its angle with the primary beam is zero; the primary rays then pass directly down the chamber. It is, of course, necessary that the window of the chamber should be large enough to include the whole cross-section of the primary beam.

The greater intensity of the primary rays necessitates the addition of a large capacity to the primary electroscope system. The ratio of the capacities of the two systems can be obtained by the method described by Norman Campbell. Let C_p, C_s be the capacities of the primary and secondary systems, and D the ratio of their rates of charging up. Then if P is the intensity of the primary radiation, $P/I_{\pi/2} = DC_p/C_s$.

It must be noted that $I_{\pi/2}$ is not the whole scattered radiation between the angles $\frac{1}{2}\pi - \delta$, and $\frac{1}{2}\pi + \delta$, as the aperture of the ionisation chamber does not completely surround the primary beam. If ϕ is the angle subtended at the radiator by the length of the aperture (at right angles to the plane of measurement), the whole intensity of the radiation scattered between these angles is greater than $I_{\pi/2}$ in the ratio $2\pi/\phi$.

In order to eliminate the correction for absorption of the rays the radiator was inclined to the primary beam at an angle of 45°. The paths of the primary and secondary beams were then equal in the radiator. The effective thickness of the radiator (waxed filter paper) in this position was 0·495 cm.

The intensity of the scattered radiation has been shown to be proportional to the thickness d of material traversed by the primary rays. We may therefore write

$$S = kdP,$$

where k is a constant which we may call the coefficient of scattering. Substituting from above we have,

$$k = \frac{1}{d}\frac{S}{P} = \frac{1}{d}\frac{2\pi}{\phi}\frac{I_{\pi/2}}{0{\cdot}065}\frac{1}{P} = \frac{1}{d}\frac{2\pi}{\phi}\frac{1}{0{\cdot}065}\frac{C_s}{C_p D}.$$

For the present experiments we have

$$C_p = 0{\cdot}05 \text{ mf.}, \quad C_s = 0{\cdot}0000423 \text{ mf.}, \quad D = 1{\cdot}18, \quad \phi = 0{\cdot}506 \text{ radians},$$
$$d = 0{\cdot}495 \text{ cm.}$$

Inserting these values in the equation we obtain for the coefficient of scattering, k, the value **0·27**.

As the density of the filter-paper radiators is almost exactly unity, this value of k is also the value of the coefficient of scattering per unit mass. It has been thought that the mass coefficient should be independent of the nature of the radiator. Recent experiments of the author have shown that this is not the case. The amount of radiation scattered increases with the atomic weight of the radiator. Thus, the mass coefficient of the scattering being 0·27 for filter paper, for aluminium it is 0·28, for copper and nickel about 0·9, and for tin as high as 1·5, more than five times as great as for filter paper. These results have important bearings on the constitution of the atom.

Energy of Excess Radiation.

Knowing the intensity of the scattered radiation we can calculate that of the excess radiation in terms of the primary radiation. We have shown in Table II that the ratio E/S of the excess radiation to the scattered radiation was independent of the thickness of the radiator. We have already seen that we can write S in the form kdP, where k is a constant. It follows, therefore, that we may also write the whole intensity of the excess radiation in the form

$$\mathrm{E} = fd\mathrm{P},$$

where f may be called the coefficient of the excess radiation. We can then write

$$f/k = \mathrm{E}/\mathrm{S}.$$

The value of the latter ratio is given in Table V. The corresponding values of the coefficient f are given in the last column of that table. Unlike the coefficient of scattering, it is not independent of the hardness of the primary rays, but decreases as the primary rays get harder.

With the ionisation chamber in the position $\theta = 0°$, the coefficient of absorption of the primary rays in the substance of the radiator can be found by interposing different thicknesses of the substance in the path of the primary beam. The coefficient of absorption for rays with an equivalent spark-gap of 1·5 cm. in the waxed filter paper is 0·70 cm.$^{-1}$.

Summary and Conclusion.

The secondary Röntgen radiation round a radiator, in the absence of any homogeneous secondary radiation, has been shown to be divisible into two parts: (1) the scattered radiation distributed in accordance with the expressions deduced from the usual theory of scattering, and (2) an additional or excess radiation of the same quality.

An expression has been deduced for the distribution of this excess radiation, and the constants of the expression determined for different radiators and different qualities of the primary rays.

Experiments have also been made to determine the energy of each type of radiation in terms of that of the other and of the primary beam.

It would perhaps be premature to put forward at the present moment any definite suggestion as to the nature and origin of the excess radiation. We have already noted that there is a possibility of explaining it as being due to a deflection suffered by a small fraction of the primary Röntgen pulses in encounters of a special type with the atoms of the radiator. Of the nature of such collisions we have at present no information.

On the other hand, the similarity of the distribution curves to those for a parallel beam of β-rays suggests that possibly the cathode particles which are given off in quantity when Röntgen rays fall upon a radiator may play some part in the production of what we have called the excess radiation. From this point of view, the excess radiation would be due to the retransformation into Röntgen rays of some fraction of this secondary cathodic radiation. That some such transformation must take place seems certain. Further examination of the hypothesis, however, shows that, in order to make it fit the curves, further assumptions must be made, for which there is at present little evidence. Experiments are in progress to test these points. Pending their completion, it is, perhaps, not desirable to develop the suggestion further.

In conclusion, I have pleasure in expressing to Prof. Sir J. J. Thomson my thanks for his interest in these experiments.

Contributions to the Study of Flicker.—Paper III.

By T. C. Porter, M.A., D.Sc.

(Communicated by Lord Rayleigh, O.M., F.R.S. Received January 2,—Read April 25, 1912.)

Since the last papers* the research has been continued at intervals through the nine years. Some numerical errors on pp. 325 and 327 in the last paper have been detected by the author, but nothing which in the least degree alters the main results of that paper, viz., that the number of revolutions per second which a disc having a white sector w, and a black sector $360^\circ - w$, must make in order that the flicker may just vanish, under an illumination I, is given by an equation of the form

$$n = a + b \log w (360 - w),$$

a being a constant, and b of the form $c + d \log \mathrm{I}$, where c and d are constants. If the disc is considered to be under unit illumination when lighted by a standard stearine candle, burning 8·273 grm. of stearine per hour, at a distance of 4 metres; that is, if I is taken to be 1 under these conditions, then, from the combination of the series of observations described in Papers I and II, with many others made since, it follows that the numerical value of n is determined with a very fair degree of accuracy to within at most three revolutions per second, and generally within one, from the equations

$$n = 10{\cdot}7 + 12{\cdot}57 \log \mathrm{I}, \text{ for discs half white, half black,}$$

and

$$n = -27{\cdot}83 + (8{\cdot}57 + 2{\cdot}79 \log \mathrm{I}) \log w (360 - w), \text{ when the angle of the white sector is } w^\circ.$$

These two equations hold only for illuminations *above* 3·98, *i.e.* that given by the candle at 2 metres distance.

For illuminations *below* 3·98, the two corresponding equations to be used are, for the $w = 180^\circ$ disc,

$$n = 17{\cdot}6 + 3{\cdot}469 \log \mathrm{I},$$

and for discs with a white sector w, other than 180°, the equation

$$n = -38{\cdot}6 + (12{\cdot}4 + 0{\cdot}77 \log \mathrm{I}) \log w (360 - w)$$

gives satisfactory values for white sectors larger than 60°, but not so consistent with experimental results in the case of smaller white sectors. A number of careful experiments were made to determine whether the suspected sudden change in the slope of the straight line expressing the variation of *n* with log I was real or not (the break is shown in Paper II, fig. 2), with the result that it is fully confirmed, the line being certainly broken, apparently sharply, at very approximately illumination 4, *i.e.* of the candle at 2 metres. This shows well in fig. 1 of the present paper, the details for the various new points being given, without omissions, in the accompanying table.

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* 'Roy. Soc. Proc.,' vol. 63, p. 347, and vol. 70, p. 313.

Source of light.	Distance from disc, in mm.	Illumination of disc.	Log. of illumination.	Note given by 24 holes in rim of disc as described at the time.	Revolutions of disc per sec.
Screened candle ...	4240	0·0596	$\bar{2}$·775	D$_{288}$, "a little sharp"	12·0
" ...	2998	0·119	$\bar{1}$·076	F, "exactly"	14·5
" ...	1554	0·449	$\bar{1}$·653	G$_{384}$, "exactly"	16·0
Unscreened candle	4240	0·89	$\bar{1}$·949	A, "1 or 2 vibrations per sec. ♭"	17·4
"	4019	0·99	$\bar{1}$·996	A below C$_{512}$, "3 vibrations per sec. ♯"	17·9
"	3440	1·35	0·131	A below C$_{512}$, "about 7 vibrations ♯"	18·0
"	3000	1·77	0·250	B♭ below C$_{512}$	19·0
Screened candle ...	647	2·56	0·408	B, "a very little ♭"	19·7
Unscreened candle	2027	3·89	0·590	B, "a very little ♭"	19·8
"	2000	4·00	0·602	B below C$_{512}$	20·0
"	1850	4·68	0·670	B below C$_{512}$	20·0
"	1500	7·11	0·852	C, "about 5 vibrations ♯" ...	21·5
"	1392	8·26	0·917	D, "5 vibrations per sec. ♭"	23·7
"	1000	16·00	1·204	E above C$_{512}$, "exactly"	26·6
"	428	89·42	1·951	G♯ above C$_{512}$........................	33·5

The details of the observations for the other points on fig. 1 have been given in Paper II, p. 319.

The angle made with the axis of X by the upper part of the line, given as 39° in Paper II, seems to be more accurately represented as 38° 30′, whilst that by the lower, conjectured from the few readings made for Paper II to be 82° 30′, is found to be very nearly 71°. The experimental details and precautions observed were the same as those already described. To produce the lower illuminations, a single thickness of filter paper was placed in front of the standard candle, so as to cut off part of its light, and the brightness of the residual light was found to be 0·067 c.p., the paper at 647 mm. distance giving the same illumination as another (tested) standard candle at 2500 mm.

The lowest value of *n* at which flicker on a half-white disc was observed to disappear was 5, in a room almost completely dark, and after resting the eyes in total darkness for more than an hour, and then by averted vision.*

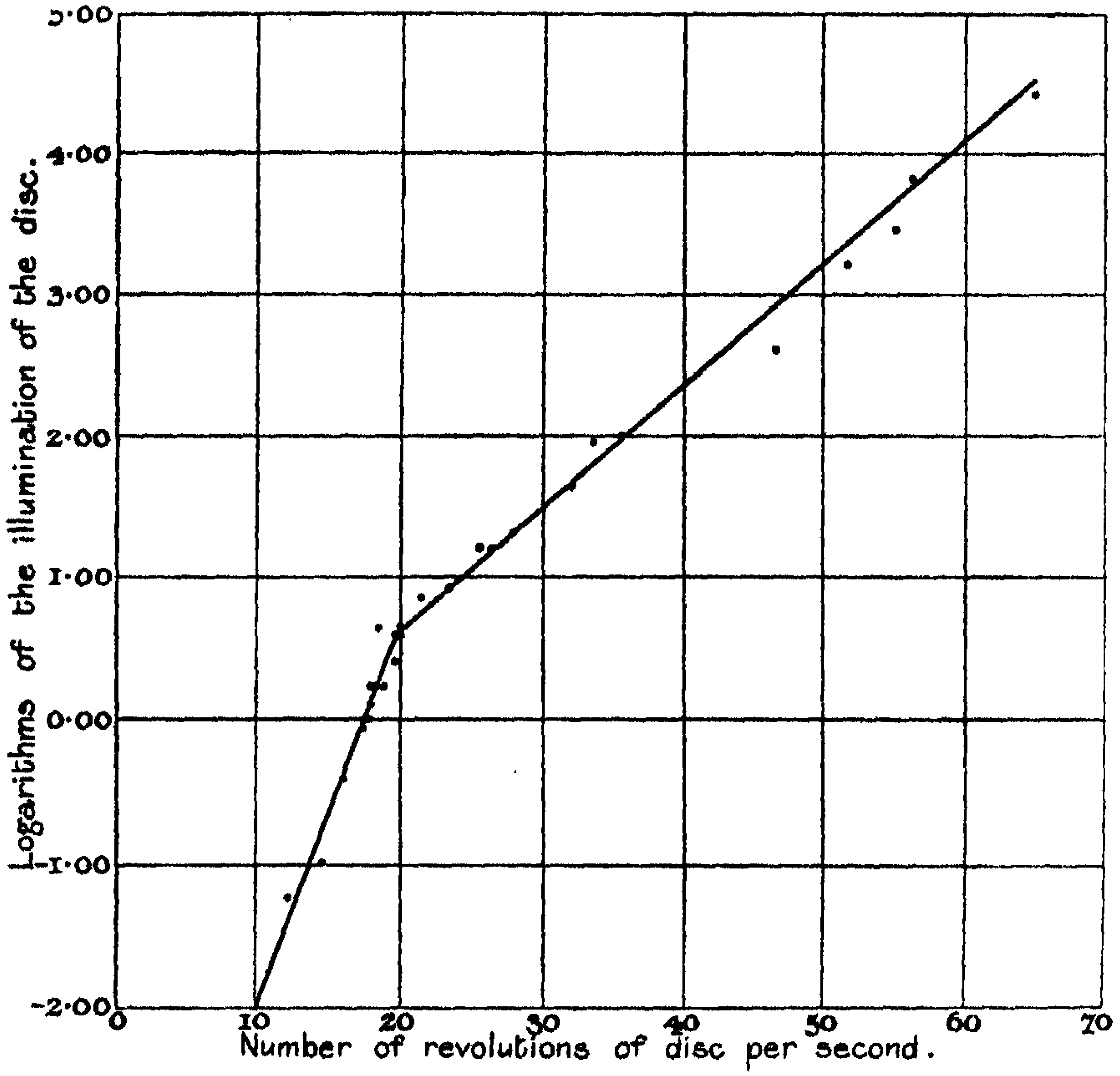

FIG. 1.

The cause of the above-mentioned remarkable discontinuity can only, at present, be conjectured in the light of experiments to be presently described. It cannot well be due to the cessation of the expansion of the pupil of the eye as the illumination falls, for it is evident that this expansion tends to keep the retina better illuminated, and therefore to make *n* fall more slowly; that is, if the pupil ceased to expand, *n* would fall more rapidly with decreasing illumination, whereas, whatever be the cause of the change in the line, it is one which makes *n* fall more slowly.

Experiments to determine the law connecting the diameter of the pupil with the illumination have been begun; it seemed desirable to fix, if possible, the limit to the expansion; to this end the eyes to be examined were kept in a pitch dark room for periods varying from 20 minutes to an hour and a half, and then photographed by a flash of light too rapid for contraction of the iris muscles to take place during so short a time. Two methods were used: (*a*) an explosive magnesium-chlorate mixture, fired by electricity, and (*b*) by a fast photographic shutter, working on a lantern nozzle, and focussed by the lantern condenser, so as to give an intense illumination. Fig. 2 was taken by (*a*), which, if successful, gives the brightest photographs, but it fails in some instances, presumably either from insufficient mixing of the

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* *Vide* Paper II, p. 315.

FIG. 2A.

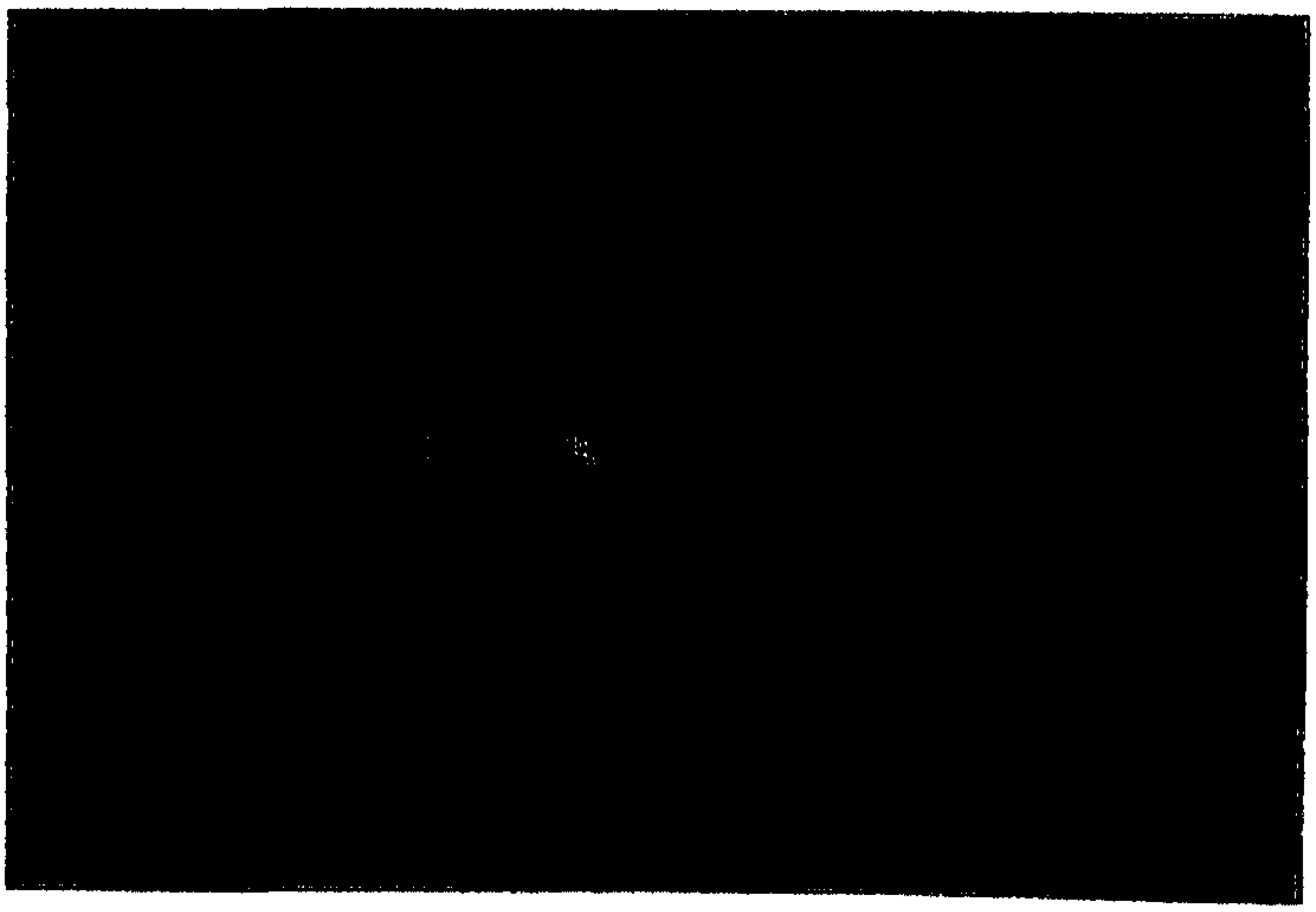

FIG. 2B.

powder's constituents, or from the little heap of combustible having a "tail," which prolongs the "exposure." Seven different pairs of eyes were tried, with the result that the ratio of the diameter of the iris's outer circle to that of the pupil varied from nearly four-thirds to three-halves. The last mentioned will be found to be that in fig. 2. Attempts were made at first to measure this ratio under various degrees of illumination with a telescope and micrometer eyepiece, but the results were unsatisfactory. At low illuminations the limit of the dark pupil was very hard to see, and made almost invisible by the necessary artificial illumination of the spider lines, and, at higher values of I, the pupil was never steady enough, not only moving slightly, as a whole, whilst measurements were being taken, but also constantly changing its diameter slightly, now expanding, now contracting. The flash-light method is free from these objections; the eyes can be fixed on the white disc while they are photographed, the flash being made well to the side of the disc. The measurements taken so far only show that it is unlikely that the variation of the pupil's size at illuminations less than 16 plays any considerable part in the form or dimensions of the curves given.

The sectors of white and black on a disc may be arranged symmetrically or not. If there be only one sector of each sort, it may now be said that we know the rate at which the disc must be rotated under a given illumination in order that flicker may just vanish, for all possible values of the two sectors. How is this rate affected if there are more than two sectors? A definite answer can be given for one class of disc, viz., that in which there are the same number of sectors of white and black, and all of these of the same angle. Take, for example, a disc with four sectors of 90°, alternately white and black. It is clear that, at any rate of rotation, such a disc presents to the eye exactly the same stimulus and rest periods as a disc half white, half black, if the four-sector disc be made to go round at half the speed of the other; consequently, if it require, say, 40 revolutions per second to make a "half-and-half" disc's flicker vanish under a given illumination, it will require exactly 20 revolutions per second to make the disc in quarters show no flicker at the same illumination. Experiment shows that this is exactly true; under all illuminations, a disc in quarters becomes flickerless at exactly half the speed necessary for a disc in halves. A disc of six 60° sectors, three white and three black, is flickerless at one-third the speed of the half-and-half when the latter is just flickerless (the illumination being the same). The following is a typical experiment: A disc was divided into three concentric rings, the innermost made of 180° white and 180° black; the next ring, with 90° sectors, alternately white and black; whilst the outermost ring was divided into 12 equal sectors, six white, six black. The disc had 24 holes in its rim, and the notes it gave were:—

(*a*)	For disappearance of flicker in the innermost ring...	A above C_{256},
(*b*)	For the middle ring	A below C_{256},
(*c*)	For the outermost ring..	D above A_{128},

all three notes being sounded very exactly.

Another experiment was made with a white disc with two concentric rings, the inner a half white, half black; whilst the outer was divided into 24 equal sectors, alternately white and black. On rotating this under a certain illumination, the flicker for the inner circle vanished at D above C_{1024}, or 1152 vibrations per second, whilst the flicker for the outer ring vanished at G below C_{128} (= 96 vibrations per second). Now $1152 = 12 \times 96$.

The number of revolutions per second necessary for flicker just to vanish under a given illumination is therefore in all perfectly symmetrical discs inversely proportional to the number of sectors.

This fact has proved very useful in the present research, for when examining the flicker-vanishing rotation necessary for a half-and-half disc under high illuminations, the speed of rotation of the disc is very great, and if the disc has, say, 12 holes, the pitch of the note emitted is high. This means that any error in judging the pitch of the sound makes a large error in the value of n inferred. If the number of holes in the syren is diminished, the sound it gives is too much enfeebled. The pitch of a note is most correctly estimated when it lies within the register of the experimenter's own voice. The remedy for this difficulty with high speeds is to use a disc with two or three times as many sectors; flicker will then disappear at a half or a third the speed necessary for the half-and-half disc, and then, by the above law, we can calculate the speed of the latter.

The law for perfectly symmetrical discs is also useful if the flicker disc is used to measure bright illuminations such as obtain out of doors in summer weather. These can be estimated, with a near approach to accuracy, and without requiring any great speed (though it *must* be even), if a disc with 45° sectors be used, alternately white and black.

Asymmetric discs, with four or more sectors.—The exact general law connecting n and the number and distribution of the sectors has not yet been found, but the following facts have been proved:—

(*a*) The flicker on the asymmetric disc always vanishes at a higher rate of rotation than on the perfectly symmetrical disc of the same number of sectors, and the same sum of the white sectors' angles.

Thus a disc was made up of the four following sectors taken clockwise in order round the disc, 120° black, 90° white, 60° black, and 90° white, whilst the central part of the disc was a circle with four equal sectors of 90°, alternately black and white. The rates of rotation for flicker to vanish in these two arrangements were as 3 to 2, the asymmetrical needing the higher speed.

Another asymmetric disc consisted of four white sectors of 45°, whilst between these white sectors came, in order, black sectors of 60°, 30°, 60°, and 30° respectively. The corresponding symmetrical disc, occupying the central portion of the other, is all 45° sectors, alternately black and white. The relative rates of rotation of these two arrangements were also, as 3 : 2, and also just half the rates necessary for the corresponding discs in the last experiment The reason for this last fact is, obviously, that the corresponding discs in the two experiments are similar, but have twice as many sectors in the second case.

(*b*) The direction of rotation makes no difference to n with an asymmetric disc. To ascertain this it is necessary to make the conditions of illumination, etc., exactly the same in the two cases, and this is very difficult to do in practice, and so the device shown in fig. 3 was resorted to. The inner circle, going round it *clockwise*, shows 120° white, 120° black, 60° white, 60° black; the outer circle, going round it *in the same direction*, shows 60° black, 60° white, 120° black, 120° white, which is the order of the sectors of the inner circle taken in the reverse direction, so that by rotating this disc we get, under exactly the same conditions, the effect of rotating the asymmetric disc first one way, and then the other, under similar conditions. The result of the experiment is that, until flicker vanishes, the "oppositely rotating" arrangements present a strikingly different appearance; but each becomes flickerless at the same moment, and at that moment of precisely the same even grey, the same grey as that of any other disc which is, on the whole, half white and half black, and under the same illumination.

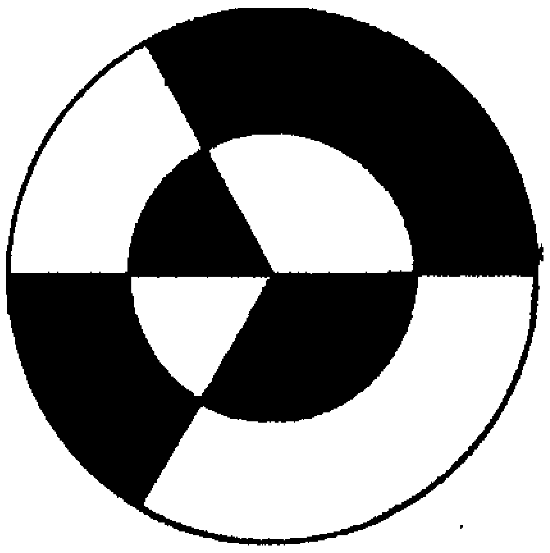

FIG. 3.

At this stage of the enquiry it was considered necessary to verify experimentally that a disc, half black, half white, rotating *flickerless* under illumination 2, looks precisely the same grey as a wholly white disc (made of the same material) under illumination 1.

The two discs were arranged at the proper calculated distances from the source of illumination, and viewed so that the nearer overlapped the more distant, and also so that the background to both the discs was black (so that any contrast effects might be the same for both). The two discs seemed like one, and when viewed through a tube which cut off the background, it was impossible for the observer to tell where one disc began and the other ended.

In the same way it was experimentally shown that the grey of a black-and-white disc, when flickerless under illumination I, appears always to match the all-white disc under an illumination $w \times I/360$, where w is the sum of the angles of the white sectors. It follows from this that the apparent luminosity of all black-and-white discs under the same illumination is the same, if w is the same; *but the converse is not true*, the apparent luminosity of two flickerless discs under the same illumination may be precisely the same, and yet the angle of the black sector may be different in the two discs; indeed one disc may be entirely white, and the other may have a black sector by no means small under some conditions of illumination, and yet these two may, to the eye, form a perfect match, when flickerless.

The next experiments were, therefore, undertaken to measure the magnitude of the black sector which could be placed in a white disc, rotating so fast as to be quite flickerless, without producing any appreciable difference to the brightness (albedo) of the disc. For the sake of brevity such a black sector will be referred to as a vanishing sector, and its magnitude in degrees as m. A white disc was prepared with a concentric broad black ring upon it, and this was dovetailed, after Maxwell's plan, with another wholly white disc made from the same cardboard; thus a variable sector of black could be produced with white on each side of it. If the black sector were greater than could completely vanish on swiftly rotating the disc, the appearance presented was of a more or less dark grey ring on a white ground; when, however, the breadth of the black sector was below a certain magnitude, no such grey ring could be seen, the disc appeared of uniform brightness.

It was manifestly of great interest to see whether Weber's law would hold in this case, *i.e.* to find out whether the width of the vanishing black sector would be 1 per cent. of the total stimulus given by the white of the disc. This would mean that, *at all illuminations*, a white disc would not be rendered appreciably darker by a sector of 3·56° of absolute black. On a bright day in a well lit room, 4° of Indian ink (which had been proved to reflect 15 per cent. of white light) just vanished; whilst at 1·25 metres from a powerful arc light, 3·6° of this same black disappeared—so that for ordinary daylight illuminations, Weber's law may be said to hold good, but it was soon found that *as the illumination of the disc is lowered below these, the magnitude of the vanishing black sector grows.*

If m be the angular magnitude of the black sector, I the illumination, and a and b constants, the equation connecting them was found to be $= a - b \log I$.

Several very careful determinations of the value of m for different illuminations were made; the results of three typical ones can be seen in fig. 4. The points marked 1 were made by a careful observer, who, however, took no very special precautions to secure a steady state of the retina: only (i) avoiding looking at the disc except when necessary; (ii) never looking at the illuminant; (iii) shutting his eyes and covering his head with a black velvet cloth when a moderate light was used in the room for the purpose of reading the distance of the disc from the illuminant. It will be seen that the readings are very consistent, and are all greater than in the other two cases. The points in fig. 4 marked 3 were obtained, on the other hand, by using every precaution experience has suggested for securing extreme sensitiveness of the retina, and also for keeping it constant. The observer, after more than an hour in a very feeble light, spent half an hour in total darkness, and except when he inspected the very faintly illuminated disc, each time fainter still, he remained in total darkness. About seven minutes elapsed between each reading.

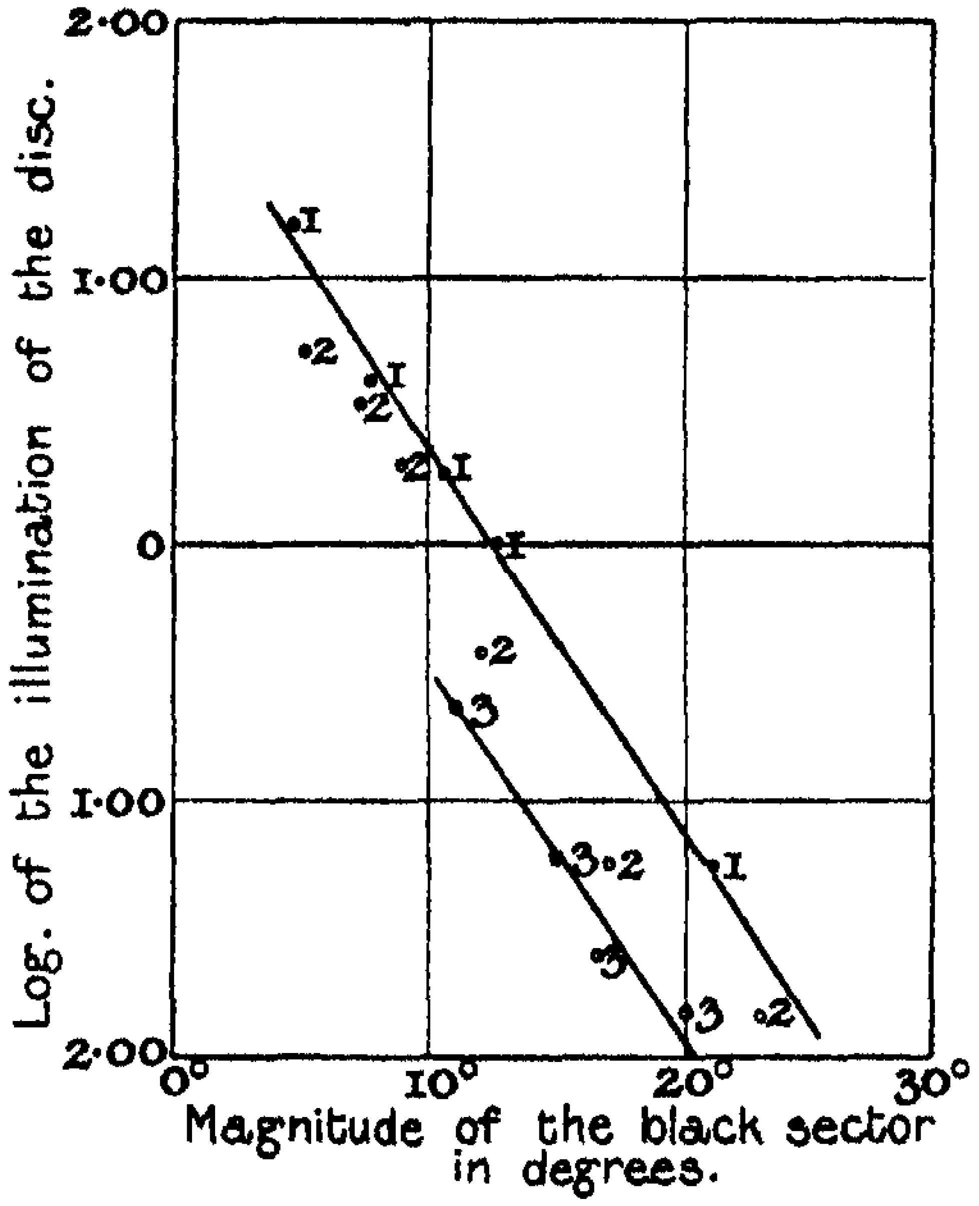

Fig. 4.

The results again are very consistent, and the line expressing the growth of the black sector with the diminishing logarithm of the illumination is very nearly parallel to the first line.

The points marked 2 are typical of the results obtained in an experiment where for the higher illuminations the observer has had no preliminary rest, has taken the readings rather rapidly, used the black cloth for the lower illuminations, but has looked accidentally at a feeble flame once or twice. The points lie between the other two sets, but they diverge much more from lineal arrangement. Unit illumination for these experiments is the same which has been used throughout the whole research, namely, that of the standard candle 4 metres off, and the lowest illumination, whose logarithm is $\bar{2}\cdot014$, is equivalent to that of the candle at a distance of 33·8 metres.

By using an illumination *much* lower than this, it was found possible to witness quite certainly the vanishing of a sector of 153·5° of black. In this case the eyes had been in darkness more than two hours, except for looking at very feebly illuminated discs for a minute or two at a time. The grey ring reappears with a very slight rise in the illumination. Whilst watching this ring on the disc, if the illumination of the disc is cut off completely and *suddenly*, the ring appears to expand outwards and inwards over the white on both sides of it, and so to render the disc black and invisible.

The feebly illuminated disc itself, much more the grey ring on it, was quite invisible to another observer, whose eyes, though fairly rested, had not been in complete darkness, so that the line of points 1 on fig. 4 must come to an end far above the end of the line for the points 3, and also the disturbance of the retina by the brightness of the disc at higher illuminations must in practice bring the line 3 to an end before it has extended far upwards.

(N.B.—In this and many other cases the observer was not the writer, and had no idea of the purpose for which he was observing; he had in every case normal and very keen sight, and was generally between 17 and 19 years of age.)

The full data for these observations will be found in the table on the opposite page.

The foregoing experiment seems to the writer of considerable importance, not only on account of the light it throws on flicker phenomena, but also because it gives a numerical measure of the power of perceiving contrast at varying illuminations: (*a*) It accounts for the small amount of detail in a landscape under feeble light, *e.g.* moonlight, and it gives a reason for the wonderful amount of detail visible in clear air under brilliant sunshine. There are, in general, two ways of making an object clear to the eye: one is to make the object appear large, either by constructing it large, or bringing it near to the eye; the other, which is very useful in exhibiting small objects to a large number of people at once, to illuminate it brightly. (*b*) The law also applies to any photometer, in which the relative brightnesses

Source of illumination.	Distance from disc, in metres.	Illumination of disc.	Log. of illumination.	*m*. No. of degrees of black sector.	Remarks.
1 c.p.	1	16	1·2	4·5	In this and the next seven Maxwell's disc method was used as described in the paper.
„	2	4	0·6	7·5	
„	3	1·8	0·25	10·5	
„	4	1·0	0·0	12·5	
Small gas flame 0·014 c.p.	2	0·056	$\bar{2}$·75	21 17 15	Eyes not rested. For condition of eyes, see paper. Eyes well rested.
„ „	1	0·224	$\bar{1}$·35	11	
„ „	3	0·025	$\bar{2}$·4	16·5	"Glimpsed 17°; couldn't see 16°."
„ „	4	0·014	$\bar{2}$·15	23 20	Eyes moderately rested. Well rested eyes, "certainly gone."
1 c.p.	0·79	5·07	0·70	5	In this and the rest of the experiments separate white discs had black sectors of the magnitudes given very carefully painted on them, and the distance from the illuminant was varied till in each case disappearance took place.
„	1·255	3·19	0·50	7·2	
„	2·070	1·93	0·29	9	
„	8·9 disc at $\cos^{-1} 0·835$	0·375	$\bar{1}$·57	12	
Arc light (unmeasured)	3	—	—	3·6	
Same	1½	—	—	3·6	

N.B.—In fig. 4 there is probably a sharp turn somewhere in the region of Illumination 10 because for all much greater illuminations *m* seems to be 3·6° almost exactly; the writer hopes to examine this point.

of two sources of light are compared by comparing (i) the brightnesses of two surfaces lit up by these sources at a distance from the illuminants, or (ii) the depth of two shadows cast by the illuminants on a screen. The experiments prove that the eye is incapable of distinguishing contrasts which lie between certain limits, these limits growing wider apart as the logarithm of the illumination diminishes. Thus, taking the photometer used in these experiments and described in Paper II, p. 316, fig. 1, where the light from each of the sources to be compared passes through one side of each of two right-angled prisms respectively, and thence to the hypotenuse, whence it is reflected "totally" on to the third side of each prism, which side is finely and evenly ground,—if the illuminants are low in power, or if the photometer is far from them, the reading on the scale when the eye judges the illumination of the two prism faces to be equal must partly depend upon the direction in which the photometer has been moved to strike the balance. Thus, in fig. 5, let L and L′ be the sources of light, P the photometer; then if P be

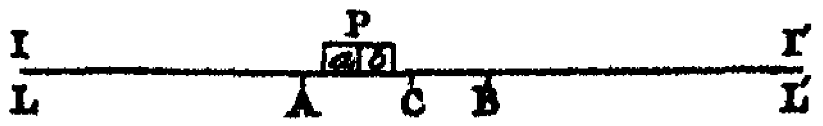

FIG. 5.

moved from left to right only, and A is the point where the faces of P *first* seem equally bright, *a* (the left face) will still in reality be brighter than *b* (the right prism's face) by an amount *m*, say, which is the same fraction of the apparent brightness of the faces of P that the vanishing black sector is of the whole of the white disc which looks as bright as P. Similarly, if P is moved only from right to left till the balance is again struck, say first at the point B, then at B *b* will be brighter than *a* by the same amount. Thus the illuminations of *a* and *b* within the space AB, which may with reason be called the "blind space," are comparable with the various invisible differences of albedo of a rotating flickerless white disc with a black sector of any magnitude from 0° to $m°$, and since we know that *m* becomes large for low illuminations, the space AB must increase with the fall of illumination and in accordance with the logarithmic law given in this paper.

Having found the points A and B in any particular experiment, we can find the true ratio of the two illuminants, for if I and I′ be the intrinsic brightness of the two illuminants at L and L′, then

At A illumination of *a* by I is $\frac{\mathrm{I}}{\mathrm{LA}^2}$,

At A illumination of *b* by I′ is $\frac{\mathrm{I}'}{\mathrm{L'A}^2}$, therefore $\frac{\mathrm{I}}{\mathrm{LA}^2}-\frac{\mathrm{I}'}{\mathrm{L'A}^2}=m$.

Similarly

At B illumination of *b* by I′ is $\frac{\mathrm{I}'}{\mathrm{L'B}^2}$,

At B illumination of *a* by I is $\frac{\mathrm{I}}{\mathrm{LB}^2}$, therefore $\frac{\mathrm{I}'}{\mathrm{L'B}^2}-\frac{\mathrm{I}}{\mathrm{LB}^2}=m$,

whence
$$\frac{\mathrm{I}}{\mathrm{I}'}=\left(\frac{1}{\mathrm{L'B}^2}+\frac{1}{\mathrm{L'A}^2}\right)\Big/\left(\frac{1}{\mathrm{LA}^2}+\frac{1}{\mathrm{LB}^2}\right);$$

and since the quantities on the right side of this equation are known, $\frac{\mathrm{I}}{\mathrm{I}'}$ is determined. Also if C is the point of true equality of illumination, and $\mathrm{LC}=x$, then
$$\frac{\mathrm{I}}{\mathrm{I}'}=\frac{x^2}{(\mathrm{LL}'-x)^2},$$
from which x can be found.

When using the photometer thus, and moving it up to A, or B, always in the same direction, it is necessary to close and rest the eyes before deciding whether it has been moved far enough, because, to take for example the determination of A, as *a* has always been brighter than *b* during this motion, the retinal fatigue caused by *a* will be greater than that caused by *b*, and it will be found that, after resting the eyes, P has to be advanced a little more. If great accuracy is required, the eyes should be rested approximately equally when the other position, B, is being found.

With higher illuminations of the photometer faces, the interval is found, as it should be, to be much smaller, and more difficult to trace. The retinal fatigue is then greater, and by far the more serious source of error.

To give the results of one of several experiments :—

Two very small gas flames were used, run from a wide branched tube, so that any possible change in gas pressure should affect both flames equally (the measuring scale was 60 inches long, and was graduated from zero on the left, this zero was 47·84 inches from I, the true zero, and 96·48 inches from I′.

Moving P from left to right.	Moving P from right to left.
28·34	30·51
26·63	27·36
26·98	27·25
25·36	27·21
4)107·31	4)112·33
26·83	28·05

I.e., AB = 1·25 inches.

The left gas flame, measured against a standard candle, gave its intrinsic brightness as 0·014 c.p. Therefore

$$\frac{\mathrm{I}'}{\mathrm{I}} \text{ (by method already given)} = 1{\cdot}58,$$

and the point C, fig. 5, is then found to be 27·47, *i.e.* 0·64 inch to the right of A, and 0·61 inch to the left of B.

Now the illumination of 0·014 c.p. at A is $\dfrac{0{\cdot}014}{(48{\cdot}74+26{\cdot}83)^2}$,

and ,, ,, ,, C ,, $\dfrac{0{\cdot}014}{(48{\cdot}74+27{\cdot}47)^2}$.

The difference between these, multiplied by 2 (because not only does the brightness of *a* diminish in moving P from A to C, but that of *b* increases in nearly the same ratio, since I and I′ are not very unequal), is the imperceptible decrease of illumination at illumination $\dfrac{0{\cdot}014}{(48{\cdot}74+26{\cdot}83)^2}$. As a percentage of this last illumination this is equal to 3·4.

Now the illumination given by the standard candle at 4 metres is the unit brightness of the disc, and the brightness of a white disc at point A in the photometer experiment is found to be 0·0608, the logarithm of which is $\bar{2}\cdot78$. On referring to fig. 4, we find the angle of the vanishing black sector at this illumination, for well rested eyes, about 17°, or corrected for 5 per cent. of white light in the black pigment used, 16°, which, as a percentage of the all-white disc, is 4·4. This tallies well with the result of the photometer experiment, when we remember that the apparent illumination of the photometer face is a little greater than that of the white cardboard at the same distance from the gas flame.

It appears from the facts expressed in fig. 4 that it is possible, and not very difficult, to express *numerically* the state of the retina as regards excitability by finding the magnitude of m, and further, that it is by no means impossible to keep the state of the retina fairly constant, even allowing for some brief but considerable changes in the illumination of the room the observer is in, provided that the state required is not that of exceeding sensitiveness; to maintain this last, very little variation can be permitted, and that must be followed by several minutes' complete rest.

To return to fig. 4. The equation which best represents the line 1 is

$$m = 12\cdot2 - 6\cdot8 \log \text{I},$$

where m is the angular width of the vanishing black sector in degrees, and I is the illumination measured in terms of the illumination given by the standard candle before described, at a distance of 4 metres.

To make plain the connection between m and n (the number of revolutions per second which must be given to a disc so that it may just become flickerless), suppose a white disc, with one black sector, to rotate very slowly before the eye. If it turn slowly enough, the excitation of the retina afforded by the white of the white sector will rise to its maximum (measured by I, the illumination the disc is under), say from A to B (fig. 6*a*), measured vertically; whilst the black sector passes, the excitation, which for brevity's sake will be called e, falls completely, to its first level, as BC. If the disc's rate of rotation be gradually quickened, it is certain that soon e neither sinks so low, nor rises so high. This can be proved by comparing the apparent white and black of the respective sectors as they pass, with the white and black of a second similar disc, kept at rest, and placed near the rotating disc so as to be under the same illumination; the differences are plain to any observer, and, as the rate of rotation is increased, become plainer still. Thus it is certain that the curve expressing the variations of e roughly resembles fig. 6*b*, and the oscillations eventually take place about the line which expresses the final value of *e*. In fig. 6*b*, drawn for a "half-and-half" disc, the final value of *e* is half its value for the all-white disc (proved already). In fig. 6*c* we have the similar curve for a disc with one white sector of 90°, the final value of *e* being one quarter its maximum value. In every case, so soon as the rise and fall of *e* become equal to the corresponding rise and fall caused by *m*, the vanishing sector on an otherwise white disc for the particular value of brightness shown by the first-mentioned disc at the moment,—then flicker vanishes. For example,—for the half-black, half-white disc in fig. 6*b*, suppose that KL is the amplitude of the variation of *e* (shown enlarged out of proportion in fig. 6*d*), when flicker just vanishes, then, if the disc is kept turning at this rate, the imperceptible variations will continue of the same magnitude as long as the disc seems of the same brightness, and if its apparent brightness diminishes from retinal fatigue or any other cause, then, since the value of the vanishing black sector increases as the brightness falls, the flicker will manifestly be further from visibility. In other words, if a disc is once flickerless, provided that its illumination be not raised, nor the rate of rotation slackened, it will remain flickerless. This is consistent with experience. Gazing at a flickerless disc never makes the flicker reappear, and it is plain that in judging whether a disc is flickerless or not, it is well to be as quick as possible.

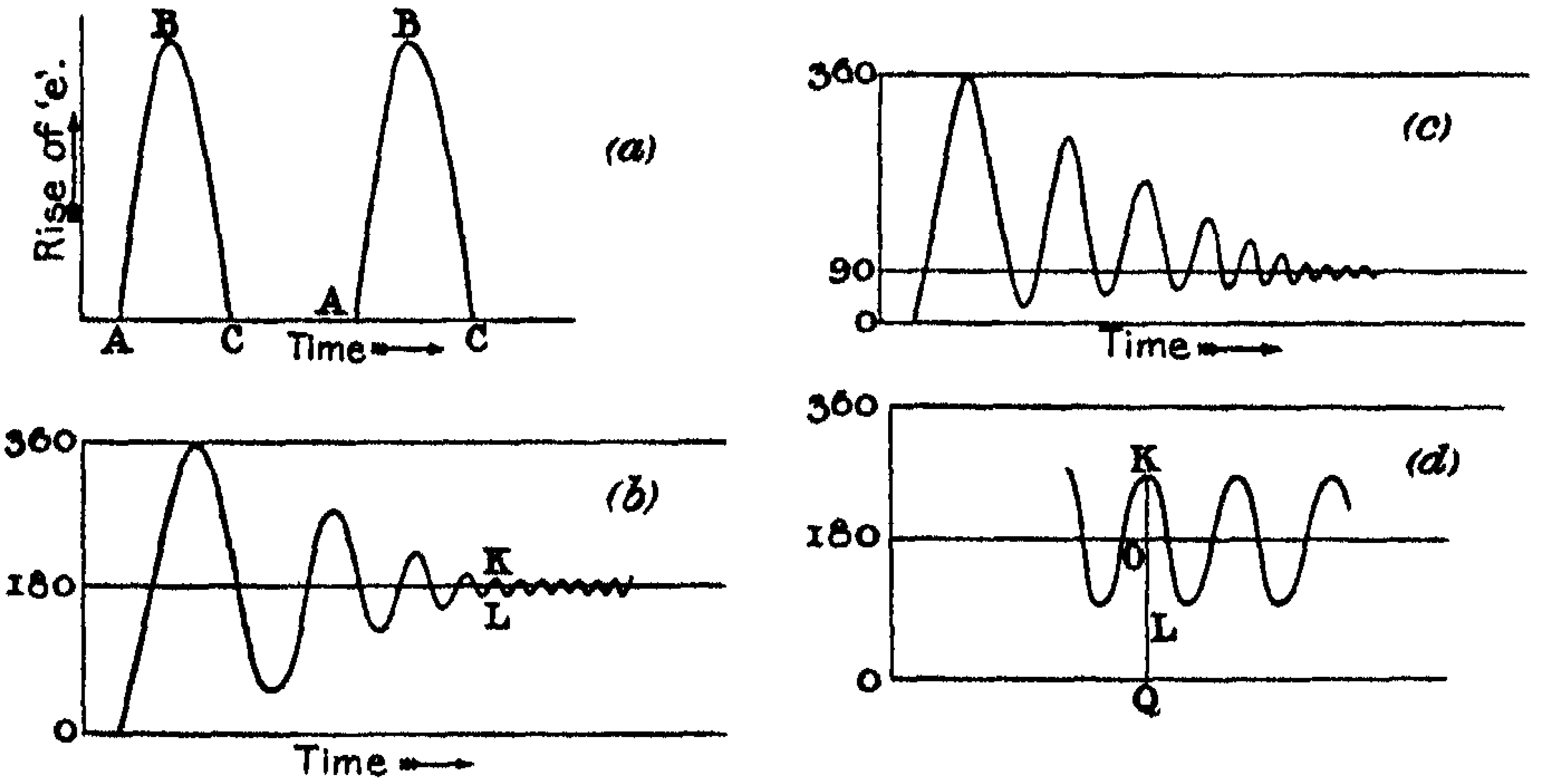

FIG. 6.

The *total* excitation caused by the passage of the white sector when flicker just vanishes is expressed in fig. 6*d* by KQ, the actual rise by LK, and the fall by KL, for when flicker just vanishes (not necessarily at any other speed) the rise and fall of *e* must be equal, for if either were the greater, the effect would be cumulative, and the disc must grow apparently brighter or darker, whereas as a fact it remains of the same apparent brightness, namely, OQ (or KQ, or LQ). Thus, if the white and black sectors are of equal magnitude, the mean rate of rise of e must be equal to the mean rate of fall of e during the passage of the white and black sectors respectively, and if the white and black sectors are of unequal magnitude then, at the rate of rotation for which flicker just vanishes (not necessarily at any other rate), the *rate of rise* of e (whilst the white sector passes) must be to the *rate of fall* of e (whilst the black sector passes) as the time the *black* sector takes to pass is to the time the *white* sector takes to pass, that is as the angular magnitude of the *black* sector is to the angular magnitude of the *white* sector. Now KL (fig. 6*d*) is to the apparent brightness of the disc (OQ) as m, the magnitude of the vanishing black sector in degrees, is to $360-m$, or, since $360-m$ is indistinguishable from 360° in brightness, to 360.

Thus, if we know m and w, and n, the rate of rotation for flicker just to vanish, we can find the rate of rise and rate of fall of e, when the mean value of e is w of the highest value the disc can give, *i.e.*, 360. Now these quantities have been measured during this investigation, and equations connecting them have been established. We can find the three above-mentioned quantities for every 10°, say, of increase of the white sector under a given constant illumination, and therefore we can find the rate of rise and fall of e when it is just reaching these mean values. *If we assume that the rate of rise and fall of "e" at a given value of "e," when "e" is not approaching a limiting value, is proportional to these rates found for a series of limiting values*, we can also arrive at a definite idea of the curve which expresses the rise of the excitation of the retina with time, when we look at a flickerless rotating or, equally well, the same white disc, or any other equally white surface, *at rest.*

It is necessary first, however, to find by experiment the size of m for discs of a variable black sector. For example, if a disc, half white, half black, is rotating under, say, unit illumination, and therefore appearing as bright as a wholly white disc under illumination 2, will the value of m be the same for the two discs, and, if not, how will it differ? We can see that it cannot be the same, for w in one case is half its value in the other, and the apparent brightness depends on w as well as on the illumination, so that a black sector of given breadth must have twice as darkening an effect on the half-and-half disc as on the other. This leads to the conclusion that m must be the same fraction of the white sector in all cases (I being constant). To test this conclusion, half a disc was painted black, and an additional black sector of 4° was added symmetrically, as shown in fig. 7.

This additional sector was found by experiment to vanish completely under an illumination of a candle of 1·2 standard candle power at a distance of 2·33 metres. If we calculate what value m must have with an all-white disc to vanish at the same illumination (3·536) using the equation given for line 1, fig. 4, we find it to be almost exactly 8°; *i.e.*, m for the white disc must be halved for the half-and-half disc which looks as bright. If, then, m is the value of the vanishing black sector for an otherwise all-white disc, then $m \times w/360$ is its value for a disc of white sector w°; *e.g.*, suppose $m = 12^\circ$ on an otherwise white disc, then on a disc with 90° white and 270° black, an additional 3° of black will vanish. On a disc with four sectors of 90° each, two white, two black, 6° will vanish, and so on, if the illuminations are such that the apparent brightnesses of all the three discs when flickerless are the same.

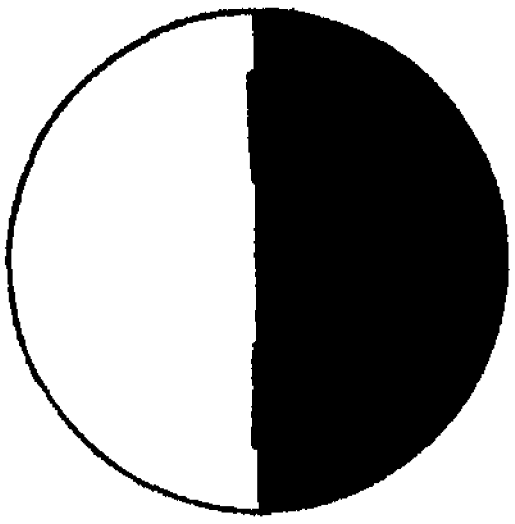

Fig. 7.

We can now deduce the form of the curve expressing the rise and fall of the retinal excitation, or, perhaps, more correctly, of the apparent brightness of a white surface, illuminated to a given degree, and suddenly presented to the eye, previously in a feeble illumination (because in the particular cases for which formulæ have been given, the eyes of the observers had not been rested in complete darkness), the fall of the excitation happening when the surface is suddenly made to disappear into the same almost complete darkness.

For the illumination of the surface, take that of the standard candle at a distance of 87 cm., so that $I = 20\cdot8$ and $\log I = 1\cdot32$.

From the equation connecting I and m, we find $m = 3\cdot3$.

From the equation connecting n, I, and w, calculate the values of n for the various values of w, from $w = 5^\circ$, 10°, 20°, etc., up to $w = 355^\circ$.*

In each case the actual rise of e (not the total rise), when the critical speed of rotation n is reached, is, as we have proved, $m \times w/360$.

To find the rate of rise of e, divide the rise of e in each case by the time in seconds the white sector takes to pass, *i.e.*, $w/(360 \times n)$.

Thus the rate required $= (m \times w/360)(360 \times n/w)$, which $= m \times n$.

To find the rate of fall of e at the same value of e: we have already proved that the rate of fall is to the rate of rise as w is to $360 - w$, so that the rate of fall $=$ rate of rise $\times w/(360 - w) = m \times n \times w/(360 - w)$.

The curve thus obtained is seen in fig. 8. The unit of time is the second,

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* The equation actually used here was

$$n = -24\cdot83 + (8\cdot57 + 2\cdot74 \log I) \log w (360 - w).$$

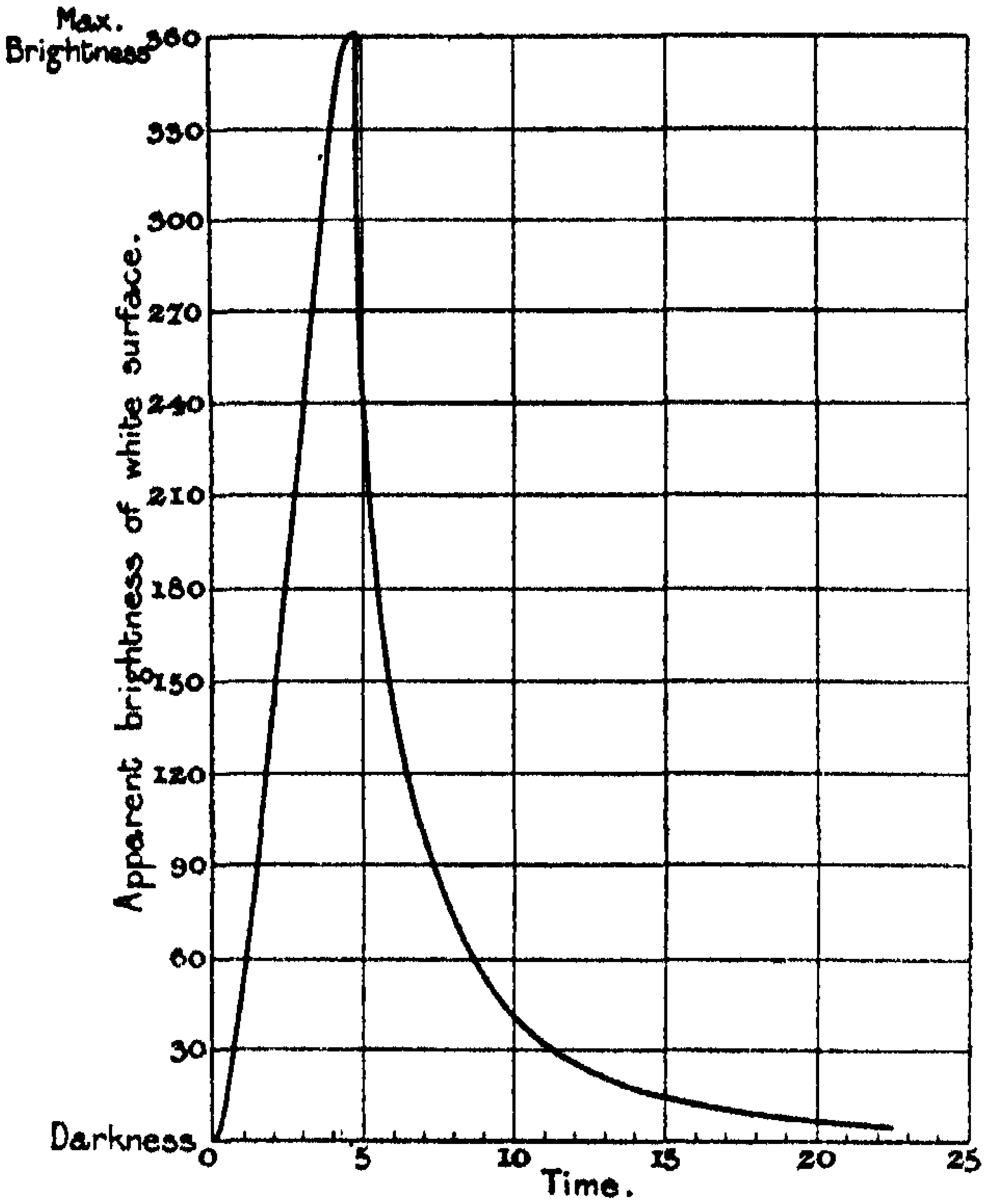

FIG. 8.

w°.	n calculated.	n observed.	Rate of rise of e in $\frac{1}{100}$ths of maximum value per sec.	$\tan^{-1}\frac{1}{10}\frac{dy}{dx}$.	Rate of fall of e in the same units per sec.	$\tan^{-1}\frac{1}{10}\frac{dy}{dx}$.
				° ′		° ′
5	14·8	17·7	48·8	26	0·68	4
10	18·37	21·3	60·6	31	1·74	10
20	21·88	22·8	72·2	36	4·35	23
30	23·87	24·3	78·8	38	7·2	36
40	25·23	25·0	83·25	40	10·4	46
50	26·24	26·3	86·6	41	13·96	54
60	27·03	27·3	89·18	42	17·8	59 30
70	27·67	27·7	91·30	42 30	22·0	65
80	28·19	28·4	93·06	43	27·2	70
90	28·62	—	94·4	43 15	31·5	72
100	28·98	—	95·7	43 45	36·8	75
125	29·63	—	97·8	—	52·02	79
150	30·06	—	99·2	44 45	70·9	82
175	30·15	—	99·5			
180	30·5	29·8	99·5	45	99·5	84 16
185	30·15	—	99·5			
235	29·68	—	97·8			
270	28·62	—	94·4	43 15	283·2	87 59
355	14·8	—	48·8	26	3464	89 50

and two of the paper divisions along the axis of X go to one second, whilst five units of retinal excitement, or apparent brightness, go to every degree along the axis of Y. It is therefore evident that, if the curve is to represent the actual rate of rise and fall of retinal excitation when one looks at a white surface of the albedo stated, and which is afterwards made to disappear, the time scale must be different from that just mentioned. From rather rough experiments made with a photographic shutter by the writer, it would appear that the whole of the rise from 0° to 360° takes about half a second: if this be true, and the assumption mentioned above (in *italics*) be correct, we must consider each of the paper divisions, of which every other one is marked in black along the axis of X, to represent one twentieth part of one second. The data for the construction of the curve are given in the foregoing table.

The Nature of the γ-Rays excited by β-Rays.

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(Communicated by Prof. E. Rutherford, F.R.S. Received February 24,—
Read March 21, 1912.)

In a previous paper,[*] it was shown that the β-rays of radium E excited γ-rays[†] in different materials, the amount increasing with the atomic weight of the substance used. It was found that the γ-radiation was largely increased when the β-rays fell on a lead screen suitably placed, and as the active material, radium (D+E+F), was mixed with lead sulphate confined in a small space, it was obvious that some, if not all, of the γ-radiation issuing from the mixture was due to γ-rays excited by β-rays in the lead impurity. It thus seemed possible that no primary γ-rays were emitted by radium E.

By using a more suitable source, in which the active material was spread in a thin layer over filter paper, it has been found that a primary γ-radiation is emitted from the active matter. This radiation, however, is much softer than that excited by the β-rays in lead. A more detailed account of these primary rays will be given later.

The main object of the present investigation was to examine carefully the question whether the γ-ray excited by a β-ray travels in the direction of the

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[*] Gray, 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 131.

[†] In the paper mentioned, the term secondary γ-rays was given to γ-rays excited by β-rays. To distinguish, however, from another phenomenon, described later, the term "excited" γ-rays is now used.

β-ray. This point is of considerable theoretical importance as it throws light on the question whether the γ-ray is a spreading pulse or corpuscular in nature. The experiments and their discussion may be conveniently divided into two parts:—

(1) A determination of the relative values of the emergent and incident γ-rays (using the usual convention) excited by the β-rays in plates of different thicknesses and different materials.

(2) An attempt to explain the results on the assumptions that the γ-ray is corpuscular in nature and that it moves in the direction of the β-ray exciting it.

Secondary γ-Rays.

Before describing the results in detail it is desirable to draw attention to an interesting effect observed when the primary γ-rays of radium E fall on elements of low atomic weight such as carbon.

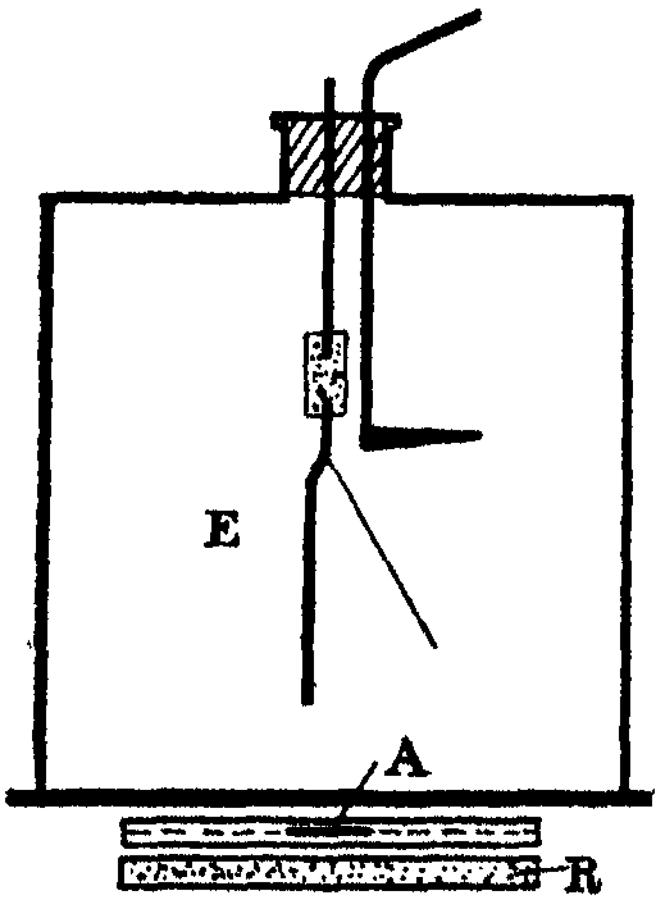

Fig. 1.

The effect is shown by the following experiment. The active material A (fig. 1) was placed between two plates of graphite, of thickness sufficient to absorb all the β-rays, and introduced under the electroscope E (the bottom of which was closed by aluminium 1 mm. thick). Readings were taken with and without different radiators R under the active material. The results are given in Table I in terms of divisions per minute of the electroscope.

From the following table it is seen that the increase in the reading is very marked when radiators of low atomic weight are used. If the penetrating γ-rays of radium had been used as a source of radiation, the

Table I.

Radiator.	Divisions per minute.	Percentage increase.
No radiator	12·50	
Graphite ...... 4·98 mm. thick	13·50	8
" ...... 12·40 "	14·40	15
" ...... 18·40 "	15·25	22
" ...... 40·00 "	15·70	25
Aluminium ... 2 "	13·10	4·80
Sulphur ...... 10 "	13·10	4·80
Iron .... 2 "	12·55	0·05
Lead .... 2 "	12·55	0·05

increase of the reading would only have been of the order of 1 per cent., so the effect observed is not likely to be one of ordinary scattering.

A provisional explanation is that characteristic radiations are emitted by the elements of low atomic weight, but more experiments are necessary before this can be definitely established. For the sake of distinction we say that primary γ-rays produce secondary γ-rays in elements of low atomic weight.

Experimental Arrangements and Results.

Some experiments will now be considered which tested whether there was any definite relation between the direction of the β and excited γ-rays. The experimental method was as follows (see fig. 2):—E was an electroscope 17 cm. cube, the bottom of it consisting of aluminium 1 mm. thick, the rest of iron 1 mm. thick. This was placed on a piece of wood W, above the poles N, S, of a powerful electromagnet. The wood was 8 mm. thick and in it was placed a piece of lead P to diminish the direct effect of γ-rays from active material placed at A. The pole pieces were covered with graphite 1·8 mm. thick. Below A′ was a piece of wood 3 mm. thick. Graphite and wood were so used, owing to the facts that comparatively few γ-rays are excited in them, and few β-rays reflected from them. LM represents the plate or "radiator" experimented on, and this was placed midway between A and A′, so that,

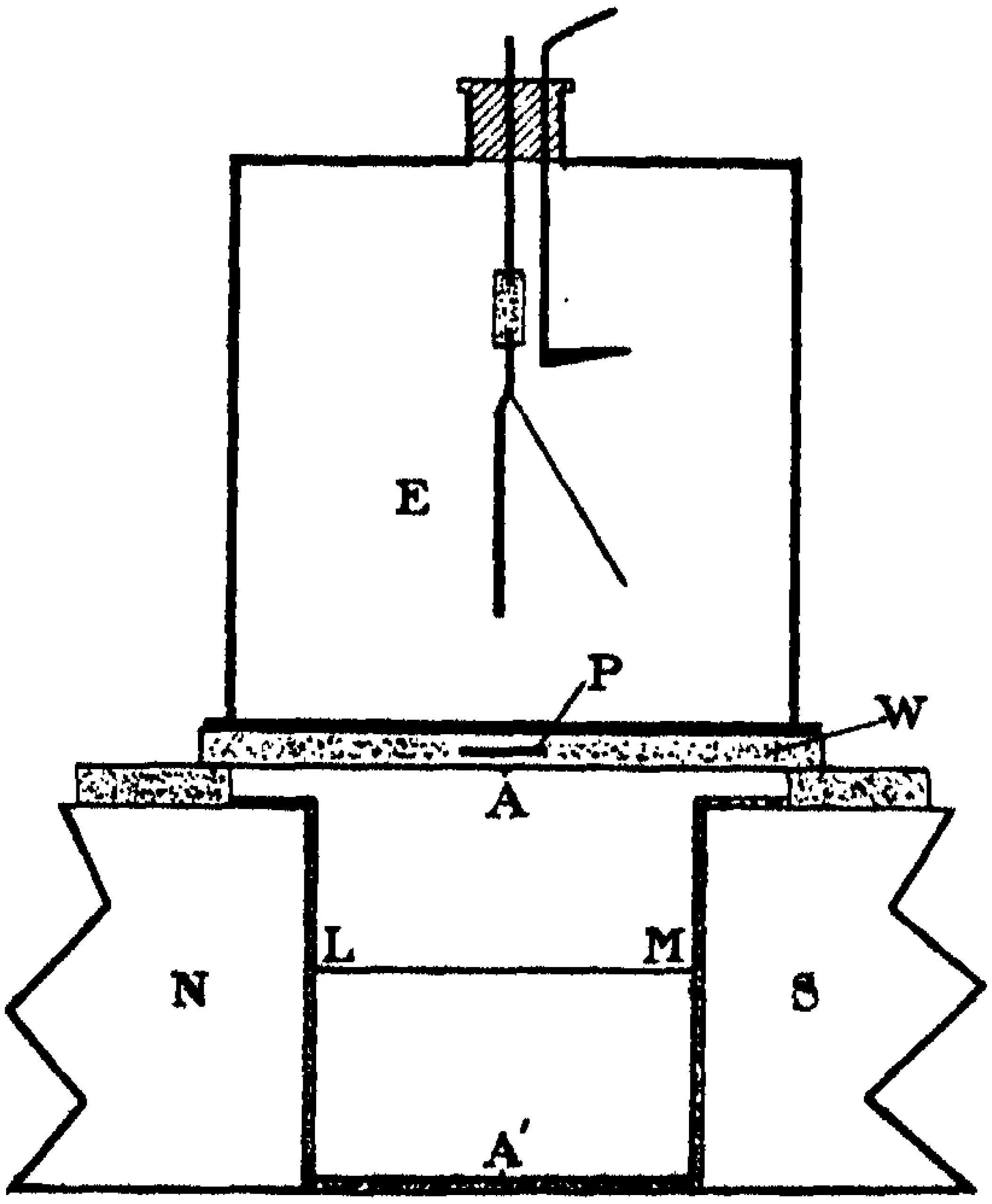

FIG. 2.

whether the active material was placed at A or A′, the intensity of β-rays striking LM was the same in either case. The dimensions of the apparatus were AA′ = 12·6 cm.; LM = 11 cm. (length at right angles to LM = 20 cm.); length of pole pieces 14 cm.

To measure emergent γ-rays, the active material was placed at A′, and readings were taken without and with a magnetic field strong enough to turn the β-rays away from the plate LM, the difference being called E′. The strength of the magnetic field used was 1100 Gauss.

To measure incident γ-rays, the active material was placed at A, and readings were taken with and without the plate LM, the difference being called I′. E′ and I′, the numbers obtained in this way, do not give us the true emergent and incident radiation, but have to be corrected for certain disturbing effects. The uncorrected values, E′ and I′, for the different radiators used are given below.

Table II.

Radiator LM.	Emergent γ-rays (uncorrected).	Incident γ-rays (uncorrected).	E′/I′.
1 lead foil	1·33	0·60	2·22
2 lead foils	1·73	1·05	1·65
3 „	2·04	1·50	1·36
4 „	2·24	1·75	1·28
5 „	2·25	1·93	1·16
6 „	2·22	2·05	1·08
7 „	2·18	2·16	1·01
9 „	2·00	2·20	0·91
Iron, 0·4 mm. thick	1·15	0·64	1·80
Paper	0·56	0·10	5·60

The mass per unit area of 1 lead foil is 0·0173 grm.

The numbers are expressed in divisions per minute of the electroscope. The larger numbers have a probable accuracy of about 2 per cent. Examples of the readings obtained are given below:—

Incident γ-rays.	No radiator	5·00
	5 lead foils	6·93
Emergent γ-rays.		
No radiator at LM.	No field	6·50
	Magnetic field	5·90
Radiator, 4 lead foils.	No field	5·00
	Magnetic field	2·76
Radiator, iron plate.	No field	4·05
	Magnetic field	2·90
Radiator, 7 lead foils.	No field	3·98
	Magnetic field	1·80

Taking the case of paper, iron and six lead foils it will be seen that the ratio of emergent to incident γ-rays is greater the lower the atomic weight. Now, in the plate LM, β-rays are scattered and some are sent back on their path. The paper reflects 8 per cent., the iron 40 per cent. and the lead foils about 70 per cent. of the β-rays falling on them,* so that in the lead many more rays in comparison are travelling in a direction opposite to their original direction. If we assume that the γ-ray moves in the direction of the β-ray exciting it, we should expect approximately the following ratios for emergent to incident γ-rays:—

Paper, 100/8, Iron, 100/40, Lead, 100/70.

The uncorrected ratios found show this order of magnitude. We can, therefore, draw the conclusion that most of the energy of the γ-ray excited by a β-ray moves in the direction of the β-ray.

To proceed further, it is necessary to make the corrections referred to above. They are few in number, and reasonably definite.

Possible disturbing effects are:—

(1) The magnetic field may affect the reading. That the magnetic field itself has no effect on the reading was shown by putting the active material below the electroscope and covering it with enough graphite to cut off β-rays. There was then no difference in the electroscope reading whether the magnetic field was applied or not.

(2) β-rays from the screen LM, which strike the bottom of the electroscope, may excite γ-rays and so increase our measure of γ-rays. This was corrected for as follows:—The active material was placed at A′ and readings were taken with and without a magnetic field, there being no radiator at LM. The difference (w) gives the production of γ-rays (as measured by the electroscope) in the material above the plane LM. When measuring emergent γ-rays the correction applied was $w \times t$, where t is the fraction of β-rays transmitted by the plate LM. When measuring incident γ-rays the correction applied was $w \times \rho \times f$, where ρ is the fraction of β-rays reflected by the plate; f is a factor introduced because of the fact that reflected β-rays are relatively slower. In the present case

$$w = 0{\cdot}60.$$

$$f \text{ (see p. 523)} = 0{\cdot}78.$$

(3) When the active material is placed at A, γ-rays (excited and secondary) are formed in the material below LM. When the radiator LM is in position,

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* Throughout, by percentage or intensity of β-rays, is meant percentage or amount of ionisation caused by the β-rays. By strength of γ-radiation is meant the ionisation caused by that radiation in the electroscope E.

some of these γ-rays are not produced, causing the measure of incident γ-rays to be too low. The correction was found as follows:—A piece of graphite, 12·41 mm. thick, placed above A′, increased the reading by 0·20 division per minute. An experiment similar to those on secondary γ-rays showed that the effect of the γ-rays formed in the material below LM when the radiator was not in position was about one-third of this, or 0·07. To the measure of incident γ-rays a number less than 0·07 was consequently added.

The experiment on secondary γ-rays shows that there is no correction for the formation of secondary γ-rays in the iron and lead plates.

Corrections (2) and (3) are the only ones that have to be considered. We, therefore, get our true emergent and incident γ-rays (E and I, say) from the equations

$$E = E' - 0{\cdot}60 \times t,$$
$$I = I' - 0{\cdot}60 \times \rho \times f + m \times 0{\cdot}07,$$

m being $\ngtr$, though usually taken = unity.

The corrected values of E and I are given in Table III.

Table III.

Radiator LM.	t.	ρ.	Emergent γ-rays = E.	Incident = I.	E/I.
Paper	0·02	0·08	0·56	0·05 ?	
Iron	0	0·40	1·15	0·52	2·21
1 lead foil	0·46	0·49	1·05	0·40	2·62
2 lead foils	0·266	0·61	1·57	0·80	1·96
3 "	0·178	0·65	1·94	1·25	1·58
4 "	0·112	0·67	2·17	1·50	1·43
5 "	0·074	0·69	2·21	1·67	1·33
6 "	0·050	0·70	2·19	1·80	1·22
7 "	0·084	0·70	2·16	1·91	1·18
9 "	0·016	0·70	1·99	1·95	1·02

The results for lead are shown by the curves in fig. 3. In the case of paper there is very little incident radiation. The ratio E/I found for iron, 2·21, agrees well with the ratio expected, 2·50. In the case of lead, the numbers are larger and more accurate, and an explanation of the results has been obtained by our assumption that the γ-ray is corpuscular in nature, and moves in the direction of the β-ray exciting it.

Let us suppose that the plate ABB′A′ (fig. 4) represents the plate under examination, and XX′ the source of β-rays. Near any point P of the plate, β-rays will be moving in all directions. We call β-rays moving from below any plane CC′ to above it "forward" β-rays, and signify them by the letter R.

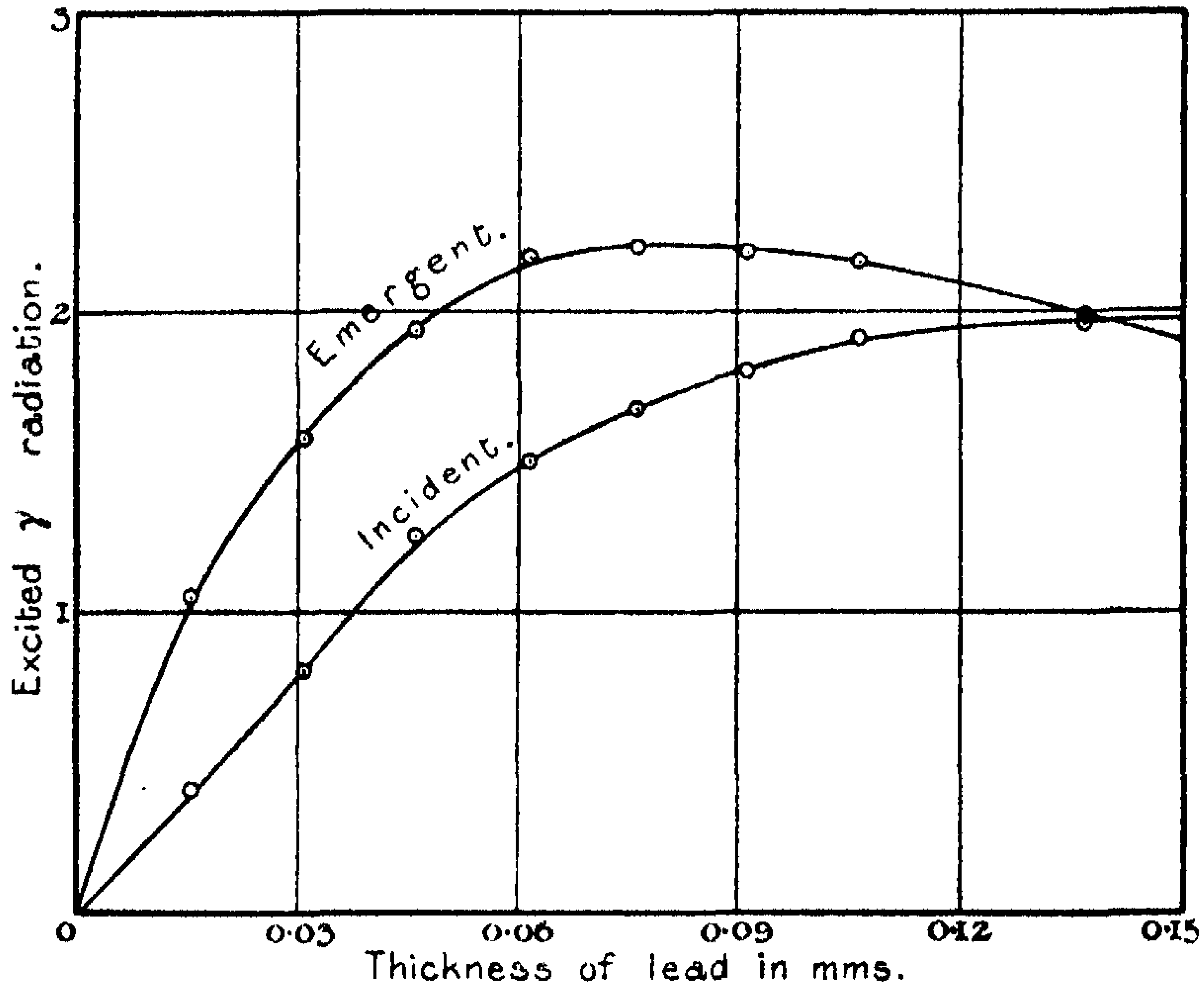

FIG. 3.

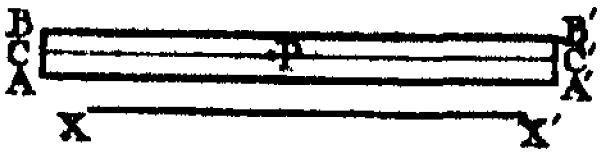

FIG. 4.

β-rays moving in opposite directions are called "backward" β-rays, and are signified by the letter r. If $AB = A'B' = d$, the thickness of the plate, $AC = x$, and the velocity distribution of forward rays is independent of x, the γ-rays formed by them will be proportional to $\int_0^d R\,dx$, etc. If the γ-ray moves in the same direction as the β-ray we must have

$$E = k\int_0^d Re^{-\lambda(d-x)}dx,$$

where λ represents the average absorption coefficient of the rays in the plate. Similarly we must have

$$I = k'\int_0^d re^{-\lambda' x}dx,$$

λ' representing the average absorption coefficient of γ-rays formed by the backward rays, and k'/k the relative efficiency of the backward β-rays in exciting γ-rays in "thin" sheets.[*]

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[*] Throughout, a "thin" sheet is taken as one so thin that practically no β-rays are reflected from it.

We have now to find how R and r vary with x and d. We will assume, for the moment, that the velocity distribution of both forward and backward rays is the same and independent of x and d. In a layer dx, forward β-rays lose a certain amount by absorption, and also by scattering, gaining a certain amount by the scattering of backward β-rays. We therefore write

$$\frac{d\mathrm{R}}{dx} = -\alpha\mathrm{R} - p\mathrm{R} + pr \tag{1}$$

$$-\frac{dr}{dx} = -\alpha r - pr + p\mathrm{R}, \tag{2}$$

$-\alpha\mathrm{R}dx$ representing the amount lost by the forward β-rays by absorption in the layer dx, $-p\mathrm{R}dx$ the amount lost by scattering of the forward rays, etc.* The solution of these equations is given by

$$\mathrm{R} = \frac{1}{1-\mathrm{P}^2e^{-2\mu d}}\{e^{-\mu x} - \mathrm{P}^2e^{-2\mu d}e^{\mu x}\}, \tag{3}$$

$$r = \frac{\mathrm{P}}{1-\mathrm{P}^2e^{-2\mu d}}\{e^{-\mu x} - e^{-2\mu d}e^{\mu x}\}. \tag{4}$$

The rays being supposed initially to be of unit intensity, equations (3) and (4) satisfy the boundary conditions

$$\mathrm{R} = 1, \quad x = 0; \quad r = 0, \quad x = d.$$

P and μ are connected with α and p by the equations

$$p = \frac{2\mu\mathrm{P}}{1-\mathrm{P}^2}, \qquad \alpha = \frac{\mu(1-\mathrm{P})}{\mu(1+\mathrm{P})}.$$

For the fractions transmitted and reflected we get

$$t = \mathrm{R}_{x=d} = \frac{1-\mathrm{P}^2}{1-\mathrm{P}^2e^{-2\mu d}}e^{-\mu d}, \tag{5}$$

$$\rho = r_{x=0} = \frac{\mathrm{P}}{1-\mathrm{P}^2e^{-2\mu d}}(1-e^{-2\mu d}). \tag{6}$$

μ is, therefore, the term ordinarily known as the absorption coefficient, and P the fraction of β-rays reflected from a thick plate. It is known that the backward rays are slower than forward rays, and so our equations can only be regarded as approximations. We can see, however, if, by choosing P and μ properly, not necessarily the same for both backward and forward rays, we can get equations (3), (4), (5) and (6) to fit experimental results.

We will apply the equations to the results for the different lead foils. It was found that μ was given by $e^{-\mu d_1} = 0{\cdot}68$ when d_1 = thickness of a single foil. A thick lead plate reflects 70 per cent. of the rays falling on it.

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* The assumptions made are the same as those used in a theory of the absorption of β-rays given by Schmidt, 'Ann. der Phys.,' 1907, A, vol. 23, p. 671.

Taking $e^{-\mu d_1} = 0{\cdot}68$, $P = 0{\cdot}70$, and substituting in equations (5) and (6) we get

$$t = 0{\cdot}447_1,\ 0{\cdot}263_2,\ 0{\cdot}169_3,\ 0{\cdot}111_4,\ 0{\cdot}0746_5,\ 0{\cdot}0508_6,\ 0{\cdot}0343_7,\ 0{\cdot}159_9,$$

$$\rho = 0{\cdot}483_1,\ 0{\cdot}611_2,\ 0{\cdot}662_3,\ 0{\cdot}68_4,\ 0{\cdot}693_5,\ 0{\cdot}70_6,\ 0{\cdot}70_7,\ 0{\cdot}70_9.$$

The experimental values are—

$$t = 0{\cdot}460_1,\ 0{\cdot}266_2,\ 0{\cdot}173_3,\ 0{\cdot}112_4,\ 0{\cdot}0740_5,\ 0{\cdot}0502_6,\ 0{\cdot}340_7,\ 0{\cdot}158_9,$$

$$\rho = 0{\cdot}490_1,\ 0{\cdot}610_2,\ 0{\cdot}655_3,\ 0{\cdot}0675_4,\ 0{\cdot}69_5,\ 0{\cdot}70_6,\ 0{\cdot}70_7,\ 0{\cdot}70_9.$$

The suffixes 1, 2, etc., refer to the number of lead foils.

Equations (5) and (6) with the values given to μ and P therefore fit experimental results very well. It follows that equations (3) and (4) must also hold approximately. This can be seen by trials similar to the following. Suppose the plate ABB′A′ consists of two lead foils, and we wish to find the intensity of R and r in the middle of these foils, d being the thickness of one foil. We have to find R and r, for $x = d_1$ and $d = 2d_1$.

Equation (3) gives $R = 0{\cdot}588$, but one lead foil reflects 49 per cent., therefore r should be

$$0{\cdot}588 \times 0{\cdot}49 = 0{\cdot}285;$$

equation (4) gives $r = 0{\cdot}282$.

Equations (3) and (4) thus give, with reasonable accuracy, the intensity of R and r inside the lead plates.

The relative power of the backward β-rays in exciting γ-rays in thin sheets, or k'/k, was found in the following manner. The active material was placed at LM and readings were taken of the emergent radiation excited in a lead plate 0·1 mm. thick, placed just below A

(1) With nothing under the active material.
(2) With a lead plate under the active material.

In the second case the emergent γ-radiation is increased by the β-rays reflected from the lead under the active material.

The active material used was spread over filter paper about 8 sq. cm. in area and placed between two thin sheets of paper. When lead was placed under this and a magnetic field applied, the field directed some β-rays on to the lead and so excited γ-rays. For this reason, the emergent γ-radiation was measured by interchanging lead and cardboard radiators at A, first lead and then cardboard being underneath. The interchange made no difference to the intensity of γ-radiation from the active material as the cardboard absorbed so little of it. The difference of the readings was taken to be proportional to the emergent γ-radiation excited in the lead, as that excited in the cardboard was only about 8 per cent. of the difference. In this way it was found that for the same intensity of β-rays, reflected β-rays produced 0·76 of the emergent γ-radiation excited by direct rays in a lead plate 0·1 mm. thick.

The β-radiation was measured by placing the active material 10 cm. below a small electroscope. Using a bare preparation of radium E under the same conditions, a lead plate reflected apparently 73 per cent. of the β-rays. The value obtained for reflected β-rays is, therefore, probably too large, and we may take it that this will account for any mistake made in taking emergent γ-radiation proportional to the difference of the readings with lead and cardboard radiators. It may be stated that when no lead was under the active material a similar piece of lead was placed near the active material.

The result obtained does not mean that in a "thin" sheet the slower rays excite only 0·76 of the γ-radiation excited by the faster rays, as we must allow for the greater absorption of the slower β-rays in the lead plate, and also for the fact that the γ-rays formed by the slower rays will be absorbed to a greater extent in the lead.

From equation (3) we get

$$\int_0^d \mathrm{R}\,dx = \frac{1}{\mu}\frac{1}{1-\mathrm{P}^2e^{-2\mu d}}(1-e^{-\mu d})(1-\mathrm{P}^2e^{-\mu d}).$$

In the lead sheet (0·1 mm. thick), the various factors in the expression in brackets are nearly equal to unity, so that, owing to the difference in absorption of β-rays, the emergent γ-ray effect will be inversely proportional to the absorption coefficients, *i.e.* we must multiply 0·76 by μ'/μ, where μ' = absorption coefficient of the reflected β-rays in lead.

In an experiment some radium E was placed 6 cm. below an electroscope, and absorption curves were taken with and without a lead reflector under the radium E, the absorption plates being placed just under the electroscope. An analysis of the curves showed that $\mu'/\mu = 1·28$. The radium E was placed 6 cm. below the electroscope, so that β-rays reflected from the absorbing screens could not interfere with the result.

To allow for the greater absorption of the γ-rays in the lead plate, we assume that the average absorption coefficients of γ-rays are proportional to the average absorption coefficients of the β-rays.

It will appear later that in a lead plate 0·1 mm. thick (equivalent to 6·6 foils) 29 per cent. of the emergent γ-rays excited by the direct β-radiation is absorbed (see p. 524). With the assumption we have made, 35 per cent. of the emergent γ-rays excited by reflected β-rays in the lead plate will be absorbed, therefore owing to the greater absorption of the γ-rays we must multiply 0·76 by 71/65, so that in a thin sheet the reflected β-rays excite $0{\cdot}76 \times 1{\cdot}28 \times 71/65$, or 1·06 the γ-radiation excited by an equivalent amount of the direct β-rays, *i.e.*

$$k'/k = 1{\cdot}06 \text{ approx.},$$

since backward β-rays are simply β-rays reflected from the further layers of a plate. The method of finding k'/k takes into account the extra absorption of the softer γ-rays in the wood and aluminium below the electroscope E (fig. 2).

That we should find k' nearly equal to k is not very surprising, as the velocity of the reflected β-rays is not very much less than that of the direct rays. For this reason, we assume that f (p. 517) $= \mu_1/\mu_1'$ where μ_1 and μ_1' are the absorption coefficients in wood of direct and reflected β-rays respectively.

The emergent γ-rays excited by the β-rays in lead have not a definite absorption coefficient, the absorption decreasing as the rays penetrate matter. An average absorption coefficient has, however been obtained. The emergent γ-rays from four lead foils are cut down to 62 per cent. by absorption in lead 0·1 mm. thick; λ is then taken from the equation $e^{-0{\cdot}01 \times \lambda} = 0{\cdot}62$ or $\lambda = 47$ in the first tenth of a millimetre. Comparing λ with μ it is found that

$$\mu = 5{\cdot}25\lambda.$$

For incident γ-rays, an average absorption coefficient λ′ is taken, such that $\lambda' = 1{\cdot}28\,\lambda$, giving $\mu = 4{\cdot}10\,\lambda'$. We are now in a position to evaluate E and I on the assumptions mentioned. We write

$$\mathrm{E} = k\int_0^d \mathrm{R}e^{-\lambda(d-x)}\,dx, \qquad \mathrm{I} = k \times 1{\cdot}06\int_0^d re^{-\lambda' x}dx,$$

μ, P, λ, and λ' having the values given above.

k is taken so that the emergent γ-radiation from five foils will be 2·20 and the results of the calculations are given in Table IV. For the sake of comparison the experimental values found above, and also numbers calculated as before but with $\lambda = \lambda' = 0$, are given. A comparison with the last numbers shows the extent of absorption in the lead foils. It will be seen that in 0·1 mm. of lead (6·6 foils) about 29 per cent. of the emergent γ-rays is absorbed.

In the calculations, it has been assumed that the velocity distribution o the forward rays is independent of x and d. This is not exactly the case, as the β-rays transmitted through a lead plate are somewhat faster than those originally entering the plate, and there must be a change throughout the thickness of the plate.

It will be seen, however, from Table IV, that the incident γ-radiation from seven foils is absorbed to the extent of only 14 per cent., whereas 33 per cent. of the emergent γ-radiation is absorbed. This shows that most of the γ-radiation is excited in the first layers of a plate, where forward and backward β-rays have nearly the same velocity distribution as direct and reflected β-rays respectively, and equations (3) and (4) hold with accuracy. Further, k varies very little with small changes of velocity, so that if the assumption on which the calculations are based is correct, there should be a very good agreement between experimental and calculated numbers. The Table shows such an agreement, especially for four or more foils. With respect to the other numbers, the agreement is fairly good, as the numbers are more difficult to obtain accurately, and the corrections have a larger effect on the result. The ratio E/I is of the right order for these foils. We have thus very good evidence that the γ-ray is an entity which moves on in very nearly the same direction as the β-ray exciting it. Another way of expressing such a result is to say that the γ-radiation excited by β-rays in a "thin" sheet is invariably emergent.

Table IV.

Radiator.	Experimental values.			Calculated values.			Calculated values (no absorption).	
	Emergent γ-rays = E.	Incident γ-rays.	E/I.	Emergent γ-rays = E.	Incident γ-rays = I.	E/I.	Emergent γ-rays.	Incident γ-rays.
1 lead foil ...	1·05	0·40	2·62	0·92	0·38	2·78	0·96	0·38
2 lead foils ...	1·57	0·80	1·96	1·48	0·78	1·90	1·62	0·80
3 " ...	1·94	1·25	1·58	1·83	1·16	1·57	2·12	1·28
4 " ...	2·17	1·50	1·45	2·08	1·45	1·42	2·52	1·61
5 " ...	2·21	1·67	1·32	2·20	1·65	1·33	2·79	1·90
6 " ...	2·19	1·80	1·22	2·22	1·81	1·22	2·98	2·11
7 " ...	2·17	1·90	1·14	2·20	1·91	1·16	3·26	2·23
9 " ...	1·99	1·94	1·02	2·04	2·01	1·01	3·33	2·41

In Table V, numbers are given which are calculated on the assumption that only 90 per cent. of the γ-radiation, excited by β-rays which strike one side of a thin plate from all possible directions, is emergent. This is done to see if a lower limit can be assigned to the percentage of emergent γ-radiation in such a case.

The numbers are calculated from the equations

$$E = 0{\cdot}90k\int_0^d Re^{-\lambda(d-x)}dx + 0{\cdot}10k'\int_0^d re^{-\lambda'(d-x)}dx,$$

$$I = 0{\cdot}90k'\int_0^d re^{-\lambda' x}dx + 0{\cdot}10k\int_0^d Re^{-\lambda x}dx,$$

k being again taken so that the emergent γ-radiation from five foils = 2·20.

Table V.

Radiator.	Emergent γ-rays.	Incident γ-rays.	E/I.
1 lead foil	0·89	0·40	2·23
2 lead foils	1·45	0·88	1·65
3 „	1·82	1·30	1·40
4 „	2·08	1·61	1·29
5 „	2·20	1·82	1·21
6 „	2·22	1·95	1·13
7 „	2·20	2·08	1·06
9 „	2·04	2·19	0·93

The ratio E/I (Table V) differs very much from the values given in Table III, especially for a small number of foils. Various errors in our experiments and calculations, however, may account to some extent for the discrepancy between experimental values and those of Table V. As regards the experiments, it is probable that if the ratio E′/I′ (Table III) is too high in some cases, it will be too low in others. In the calculations, the most serious chance of error lies in the value given to k'/k. The value 0·76 found above for the relative emergent γ-radiation excited by reflected β-rays in a lead plate represents the mean of several experiments, which gave results differing by not more than 3 per cent., and is thought not to be too high.

However, if we take the experimental ratio E′/I′ to be 4 per cent. and k'/k 6 per cent. too high, there will then be a rough agreement between experiment and calculation, based on the assumption that 90 per cent. of the γ-radiation in "thin" sheets is emergent. The errors are not likely to be so large and, if we take the lower limit referred to above as 95 per cent., we shall probably leave sufficient margin for error. We therefore conclude that when the β-rays of radium E strike one side of a "thin" plate from all possible directions, between 95 and 100 per cent. of the γ-radiation excited is emergent. Further discussion will be given later.

As backward β-rays are slower than forward β-rays, incident γ-rays should be softer than emergent γ-rays, and this has been proved by another experiment. The electroscope E was replaced by a box, 12·6 cm. cube, from which an electrode passed through a balance chamber to a tilted gold-leaf electroscope. The absorbing materials above the wood W (fig. 2) were a lead plate 0·1 mm. thick and an ebonite plate 1 mm. thick. The results are given below, the emergent γ-radiation from six lead foils being about 70 per cent. of the previous value (Table III).

Table VI.

Radiator LM.	Uncorrected values.		Corrected values.		
	Emergent γ-rays.	Incident γ-rays.	Emergent γ-rays.	Incident γ-rays.	E/I.
Lead (6 foils)	3·52	2·70	3·50	2·48	1·41
Iron	1·53	0·66	1·53	0·54	2·83

$w = 0·52$.
$f = 0·60$ app.

The corrections, though comparatively uncertain, are small. A comparison of Tables III and VI shows that the incident γ-radiation from a radiator is softer than the emergent γ-radiation.

Taking the emergent γ-radiation from six lead foils as 70 per cent. of the previous value (Table III), the emergent γ-radiation from the iron is 60 per cent. and the wood 35 per cent., showing that the excited emergent γ-radiation is more penetrating the greater the atomic weight.

It has been shown by several experimenters that the β-rays of radium E are not homogenous, but have velocities varying over a fairly wide range. The result obtained would be explained, if in thin sheets of different substances the slower rays produced relatively more γ-rays, the lower the atomic weight of the substance. The γ-rays formed would then be less penetrating the lower the atomic weight. This would indicate that the values of f (p. 517) are not large enough. On the other hand, β-rays of the same speed might excite less penetrating γ-rays in "thin" radiators of low atomic weight.

Taking the sum of emergent and incident γ-radiation (Table IV) for paper, iron, and six lead foils, it is seen that the radiation excited in the paper is 0·61, in the iron 1·70 (no correction for absorption), in the lead 5·00 (correcting for absorption). In the paper, at least 90 per cent. of energy of the β-rays is absorbed, in the iron 60 per cent., in the lead 35 per cent.

For total absorption of the β-rays, we would get γ-rays excited,

In paper = 0·68, In iron = 2·80, In lead = 14·30.

These numbers are roughly proportional to the atomic weight, showing that with the β-rays of radium E, the chance of a β-ray (if it spends its range in a radiator) making a γ-ray is roughly proportional to the atomic weight of the radiator.

Somewhat similar results to those obtained above have been found by Kaye* for the production of X-rays by cathode rays in radiators of the order of 0·00001 cm. in thickness. He found that the emergent X-radiation was greater in amount than the incident radiation, and also more penetrating. An analysis similar to that made above is impossible, but the main explanation of the results must be that the X-radiation tends to move in the same direction as the cathode radiation exciting it.

Theoretical Considerations.

The result that the γ-radiation excited in "thin" sheets is practically all emergent shows that, in general, such radiation, in any amount, is not formed by small deflections of the β-rays. Let us suppose AOB (fig. 5) represents the path of a β-ray suddenly deflected at O, through a right angle, giving rise to γ-radiation. It is clear that such radiation, if due to the acceleration of the particle near O, will not move in any one definite direction, and, even if it did, that direction would probably be OX. Such comparatively small deflections cannot therefore be the cause of the γ-rays, or, at least, of any large amount of such radiation.

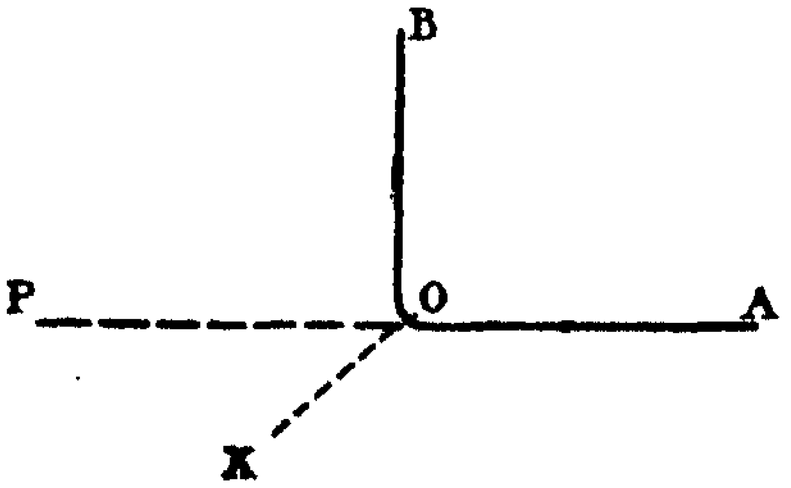

FIG. 5.

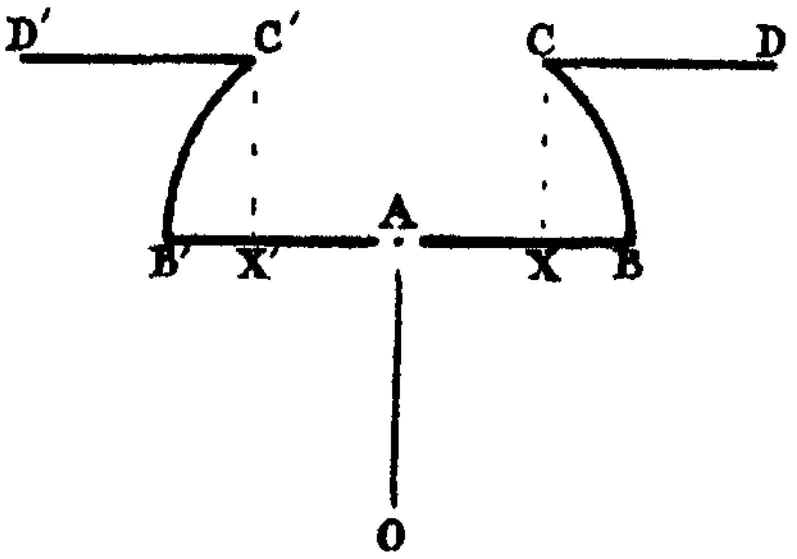

FIG. 6.

It is seen from this that γ-radiation is most likely to be produced when the β-ray is suddenly stopped.† We will, therefore, assume that the γ-ray only arises when the β-ray is suddenly stopped or loses a great part of its energy, and try to explain our results on the theory of Sir J. J. Thomson,‡ which seems, of theories akin to the ordinary pulse theory, the most suitable.

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* 'Camb. Phil. Soc. Proc.,' November, 1909, vol. 15, p. 269.

† It is considered that the β-ray stops if it forms a γ-ray in the way supposed by Bragg, as well as by loss of speed.

‡ 'Phil. Mag.,' February, 1910, vol. 19, p. 301.

In this theory, the electron has its electric field concentrated in a double cone, the vertex of which is at the centre of the electron. Let us suppose that such an electron, a β-ray of radium E moving in the direction OA, is suddenly stopped at A (fig. 6). AB represents the part of the tube at rest, CD that part moving with the original velocity, which, in the case of the β-ray of radium E, is, on an average, 0·8 that of light. The electric and magnetic forces in the kinks BC, B′C′, constitute the γ-radiation. As CX = 0·8 AC, the angle XAC is nearly 53°, and, whatever the density of energy in the kink, such radiation will not explain our results. Assuming that the energy of the kink is concentrated at C and C′, and allowing for the possible directions of the tube AB, the radiation will, on an average, move out in a circle along a cone, of which OA is axis and OC generator. It can be calculated that with such an arrangement only 82 per cent. of the γ-radiation excited by β-rays in a "thin" sheet will be emergent, the β-rays striking the sheet from all possible directions. The theory, therefore, cannot account for the production of excited γ-rays.

It seems to the writer that the assumption that the ray is an entity is correct, although the experiments do not altogether exclude the view that γ-radiation is a disturbance which spreads out as it travels along. If such were the case, however, the disturbance would, on an average, have to be confined to a cone of small solid angle, the axis of which would be the direction of motion of the exciting β-ray. With such a disturbance we have the old difficulty of accounting for the fact that the properties of X- and γ-rays do not vary apparently with the distance from their source.

On the view that the excited γ-ray is an entity there are two distinct theories—

(1) The β-ray forms part of the γ-ray and gives it its energy and direction—Bragg's theory.*

(2) The β-ray supplies the energy, but does not form part of the γ-ray, which travels on as a "bundle" of energy, without change of form. Stark† has put forward a theory of this kind. He considers the X- or γ-ray to be of the same nature as light, and obtains the direction of the radiation by considerations of momentum.

Summary.

The results of the experiments are summarised below :—

(1) The emergent γ-radiation excited by β-rays in different radiators is generally greater in amount and more penetrating than the incident radiation. It increases in penetrating power with the atomic weight of the radiator.

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* 'Phil. Mag.,' October, 1907, vol. 14, p. 429, and September, 1910, vol. 20, p. 385.

† 'Phys. Zeitschr.,' 1909, 1910.

(2) The ratio of emergent to incident γ-radiation is greater, for radiators of the same material, the thinner the radiator, for radiators of different materials thick enough to stop the β-rays, the lower the atomic weight.

(3) Results obtained point to the conclusion that the ray is an entity, the direction of which is nearly that of the β-ray exciting it.

(4) For β-rays of the speed used, the chance of a β-ray making a γ-ray is roughly proportional to the atomic weight of the radiator, provided the β-ray spends its range in the radiator.

In conclusion, the writer has much pleasure in expressing his best thanks to Prof. Rutherford for his very helpful interest in this research, and for the use of the very active preparation of radium D necessary.

The After-luminosity of Electric Discharge in Hydrogen, observed by Hertz.

By the Hon. R. J. STRUTT, F.R.S., Professor of Physics, Imperial College of Science, South Kensington.

(Received March 1,—Read March 21, 1912.)

In previous papers I have examined certain striking cases of after-luminosity in gases through which the electric discharge has been passed. The cases dealt with fall under two heads, those due to ozone, and those due to active nitrogen. I wish now to pass to a case in which neither of these substances is concerned.

Hertz* described a phenomenon of after-luminosity which he had observed in hydrogen. The method of investigation was somewhat special. A series of jar discharges was passed through a small discharge tube, with an open end, arranged inside a bell jar. It was then observed that at each discharge a stream of luminous gas was squirted from the end of the small discharge tube into the bell jar. This is apparently due to a kind of explosive action of the spark—the same, probably, as that described by De La Rue and Muller.† The method is well adapted to show the afterglow in other gases, nitrogen or air, for instance, but the immediate concern is with hydrogen. With this gas, Hertz sometimes observed a jet of blue luminosity, which was best developed at a pressure of

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* 'Wied. Ann.,' 1883, vol. 19, p. 78.

† 'Phil. Trans.,' 1880, vol. 171, p. 86.

100 mm. He considered that he had good evidence that this luminosity showed the hydrogen spectrum, but he found an unaccountable capriciousness of the effect, which sometimes refused to appear at all. He did not succeed in tracing the cause of this uncertainty. Goldstein* made similar experiments; he states that the spectrum consists of at least 10 bands, from the green to the ultra-violet, totally unrelated to the recognised hydrogen spectrum. But he believed that the glow was due to pure hydrogen.

This glow is of very short duration. I have not been able to observe it, either by the use of a rapid stream of gas, as in the former investigations, or by the simple method of looking at the vessel immediately after the discharge is stopped. Hertz's method is much more searching for detecting a glow of very short life.

The form of discharge vessel used in my experiments is shown in fig. 1, which scarcely needs detailed explanation. Jar discharges take place between the electrodes *a*, *b*, which have a spark-gap in series with them. The glowing gas is squirted into the large bulb *c*, and the glow remains continuously visible in this bulb, in a state of turbulent motion, as long as the induction coil is in action.

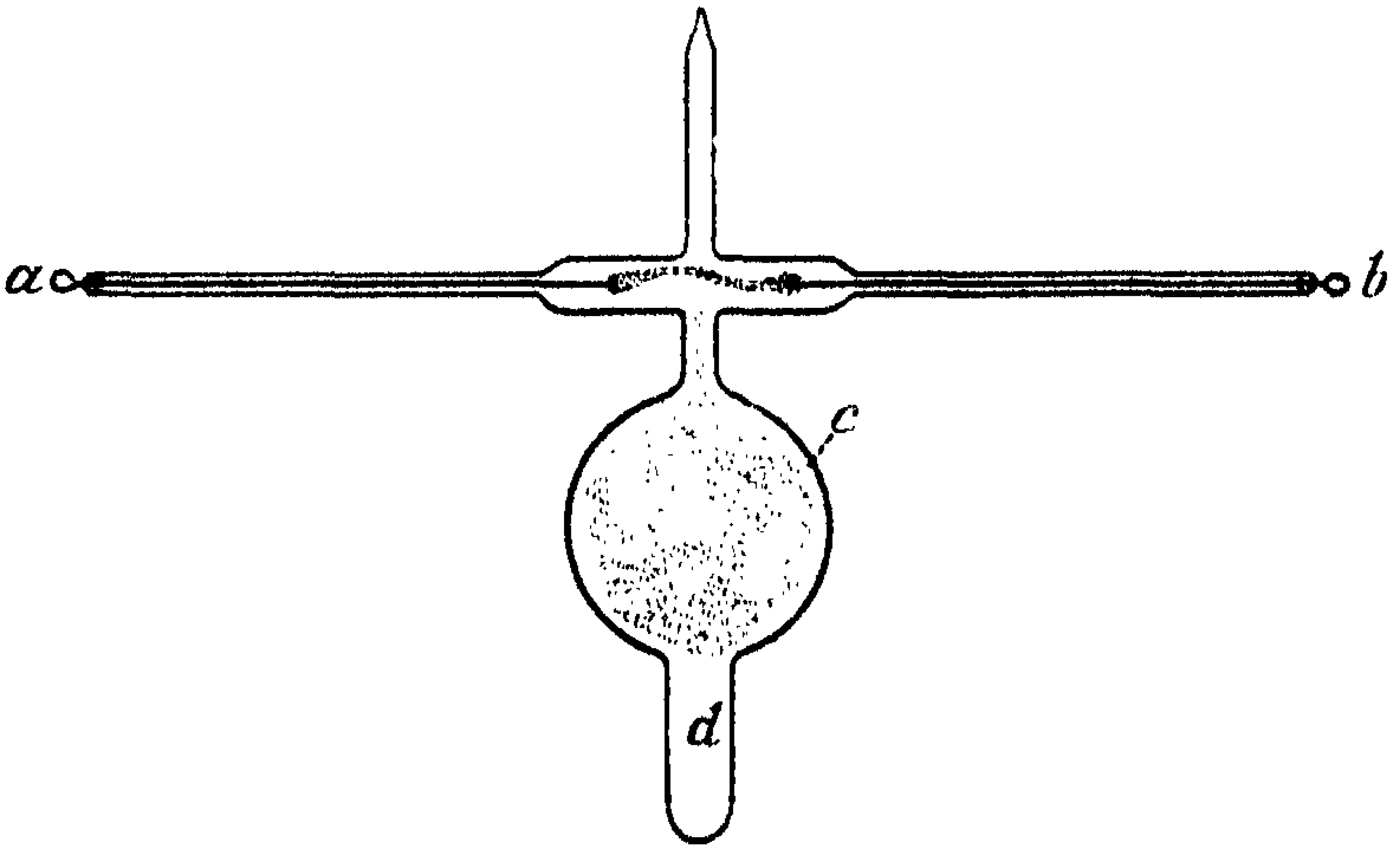

Fig. 1.

On admitting commercial hydrogen from a cylinder of the compressed gas to a pressure of about 50 mm., the blue glow described by Hertz was brilliantly developed. I never failed to obtain it in this way, and to maintain it as long as desired. The first object was to photograph the spectrum, which was readily done by means of a small quartz spectrograph, through a quartz window (not shown) in the side of the bulb *c*. The spectrum is reproduced in fig. 2, and was at once recognised as identical with the spectrum obtained when active nitrogen is passed over heated sulphur.* A photograph of the latter taken with the same instrument was an exact facsimile of that of the hydrogen afterglow here reproduced. The same bands occur in the flame of carbon disulphide, but obscured to some extent by a continuous background.

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* 'Verhand. d. Phys. Gesellsch.,' 1883, vol. 2, p. 16.

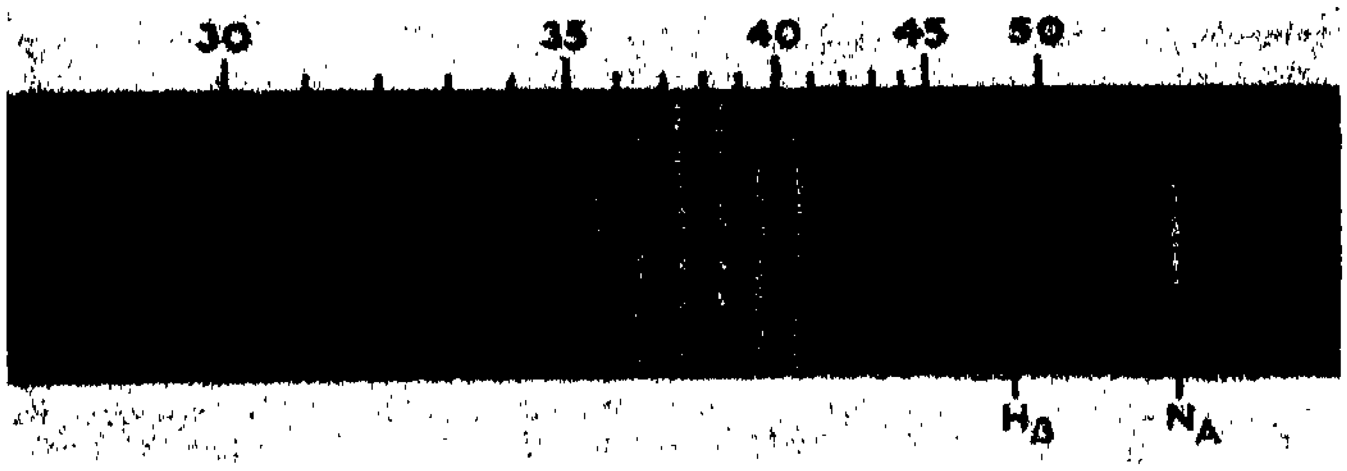

Fig. 2.

The H_β line which appears in the photograph is, no doubt, due to stray reflected light from the discharge. The sodium line was put on for reference.

The blue glow of hydrogen, then, is connected with the presence of sulphur as an impurity in the gas.

On cooling the annexe *d* of the vessel in liquid air, so as to condense out sulphuretted hydrogen (or any other sulphur compound), the glow disappears completely in one or two minutes. On removing the liquid air, and allowing the glass to warm up, it is restored to its full brilliancy. This is a striking experiment, and can readily be shown to a large audience.

In another experiment, after removing sulphuretted hydrogen by condensation, so as to get rid of the glow, a fresh quantity of that gas was admitted, amounting by volume to about one-twentieth part of the hydrogen present. The blue glow at once reasserted itself. There was some deposition of sulphur on the walls of the discharge tube, and it was found impossible now to get rid of the glow by condensation. Evidently fresh sulphur enters into combination with hydrogen under these conditions, and continually replaces what has been removed. It is clear that the quantity of sulphuretted hydrogen admitted was enormously in excess of what was necessary in order to bring in the blue glow in full intensity.

The formation of this glow seems, in fact, to be an exceedingly sensitive test for the presence of sulphur in hydrogen—a test that might with advantage be made use of by anyone requiring the purest hydrogen for determination of physical constants. The commercial bottled hydrogen above mentioned was found incapable of discolouring moistened lead test-

* Strutt and Fowler, 'Roy. Soc. Proc.,' 1912, A, vol. 86, p. 112.

paper, even when passed over it for an hour in a rapid stream. Yet this hydrogen gave the blue glow in full brilliance.

Again, a discharge vessel which had been washed out with sulphuric acid, and afterwards with water, gave the glow persistently, in spite of the treatment with liquid air, which is so successful in removing it from a new tube. Probably continual supplies of sulphur were afforded by a slight deposit of sulphate on the aluminium electrodes.

It has been mentioned that the spectrum of the blue glow is identical with that of sulphur in active nitrogen, or of carbon disulphide burning in air. Conceivably, in both these cases, the spectrum might be due to a compound of nitrogen and sulphur. It became important, therefore, to test whether nitrogen as well as sulphur was necessary to the formation of the blue glow in hydrogen.

Some charcoal was placed in the lower part (*d*, fig. 1) of the discharge vessel, and a small fragment of sulphur fused on to the glass in the upper part, near where the discharge passes. The charcoal was immersed in liquid air, and hydrogen admitted until the charcoal was saturated at a pressure of 50 mm. of mercury. The tube was then sealed off, keeping the charcoal cooled.

The blue glow remained in full intensity for an hour, after which the experiment was discontinued. If any trace of nitrogen had been initially present in the hydrogen used (and none was visible spectroscopically) it could not have failed to be removed by this prolonged exposure to cooled charcoal. Sulphuretted hydrogen was, no doubt, removed too, but its loss was made good from the solid sulphur intentionally introduced, as in one of the experiments previously described.

I conclude, therefore, that the spectrum of the blue glow is essentially a spectrum of the element sulphur. It may occur in the absence of hydrogen, as when developed by active nitrogen, and in the absence of nitrogen, as in the above experiment.

I have not succeeded in obtaining the well developed blue glow in sulphur vapour alone. It seems, therefore, that the glow must be dependent on a combination of sulphur and hydrogen with luminosity after they have left the discharge. For this to occur, one or other of the substances must be in a special condition of chemical activity, analogous, perhaps, to ozone or to active nitrogen. I have not been able to devise an experiment to decide which of the elements concerned possesses this peculiarity. The extreme shortness of its duration makes it impossible to apply the synthetic methods which have been so successful in the cases of ozone or active nitrogen. But on general grounds it is perhaps more likely that the sulphur is in a peculiar state.

[*Addition, March* 26.—Selenium and tellurium, the elements most kindred to sulphur, give similar effects.

A fragment of tellurium was placed in a discharge vessel like fig. 1, where it could get heated by the spark, and hydrogen was admitted to 50 mm. pressure. The deep blue glow due to sulphur was at first visible, but as the tellurium got heated up it was replaced by a greenish-blue afterglow, quite distinct from the former. At the same time the walls of the globe acquired an opaque deposit of tellurium. The glow showed a spectrum of narrow uniformly spaced bands from the red to the blue.

With selenium very similar effects were observed. The general colour of the glow was nearly the same as with tellurium, but not bright enough to make spectroscopic observation easy.

Arsenic was tried in the same way, as forming a gaseous compound with hydrogen. No glow was observed due to arsenic, and the glow of sulphur, originally present in the hydrogen used, was quickly destroyed. Probably the sulphur reacted with arsenic vapour and was thus removed.]

Pure hydrogen gives no afterglow whatever. In this respect it resembles pure oxygen,* and differs strikingly from pure nitrogen.†

In conclusion, I wish to express my best thanks to my colleague, Prof. A. Fowler, F.R.S., for help most kindly given in preparing for publication the photograph reproduced in fig. 2, and for advice on the spectroscopic side of the work generally.

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* 'Phys. Soc. Proc.,' 1911, vol. 24, p. 4.

† 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 219.

On the Changes in the Dimensions of a Steel Wire when Twisted, and on the Pressure of Distortional Waves in Steel.

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In the Proceedings of the Royal Society* there is an account of some experiments which I made to show that wires when twisted lengthen by an amount proportional to the square of the angle of twist, a result expected from an analysis of the strains in a finite pure shear. In those experiments it was necessary to put considerable loads on the wires.

I have now succeeded in measuring the change in the diameter of a wire when twisted, as well as the longitudinal extension, and have found that the change, a contraction, is also proportional to the square of the angle of twist. It has been now found that the change is sensibly the same for large loads and for the smallest load which could be used, when the wire was sufficiently straightened before being twisted, so that apparently the only function of the load is to straighten the wire.

To measure change in the diameter the wire was fastened at the bottom of a long narrow tube, the "wire tube," filled with water. It passed out from the top of the wire tube through a water-tight leather washer. A capillary glass tube rose vertically from an orifice in the side of the tube, into which it was cemented, and the change of the water level in the capillary when the wire was twisted indicated the change in the volume of the wire within the wire tube.

Description of the Apparatus.

The apparatus used for the measurement of the effects is shown in fig. 1, where, for convenience of representation, various parts are put into the plane of the figure, though actually they were in different planes.

An iron bracket B projected from the wall of the laboratory, and a tripod rested on it, on three levelling screws. The tripod carried a conical bearing for the twisting head-piece T. When the axis of this was exactly vertical, the tripod was fixed to the bracket by clamping screws s, s. The twisting head was provided with a circular plate P, with marks at 90° intervals, which could be set against a fixed index *i*. In practice only whole turns were given, so that only one mark was used, except in one experiment described later.

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* Series A, 1909, vol. 82, p. 546.

At the lower end of T, there was a chuck into which the upper end of the wire was inserted, and a tightening screw made a firm grip. The wire in all cases was very nearly 160·5 cm. long. At its lower end it was gripped by a similar chuck attached to a steel cross-piece C, about 29 cm. long, seen endwise in the figure.

Polished steel plates were screwed on to the vertical sides of this cross-piece near its ends. Four horizontal screws, working in brackets projecting from the wall, and with small steel balls at their ends, were screwed up so as just not to touch the steel plates when there was no twist on the wire. But when a twist was put on, the cross-piece moved up against two of the screws, and was thus fixed in position. Below the cross-piece there was a rod to which was attached another rod carrying a platform *p*, and on this weights could be placed. Each weight was in two semicircular halves. Below the platform was a lead weight S, which I call the sinker, with a volume of 1020 c.c. This hung in a can, and near the can was a water cistern, not shown, connected to it by a rubber tube. When the cistern was pulled up water flowed into the can so as just to cover the sinker and lessen the load by 1020 grm. When the cistern was let down the water flowed back into it and the load increased to its full value. This was used to determine Young's modulus and Poisson's ratio.

A table *t* was fixed to the wall independently of the bracket B, to carry the observing microscope, and the observer sat

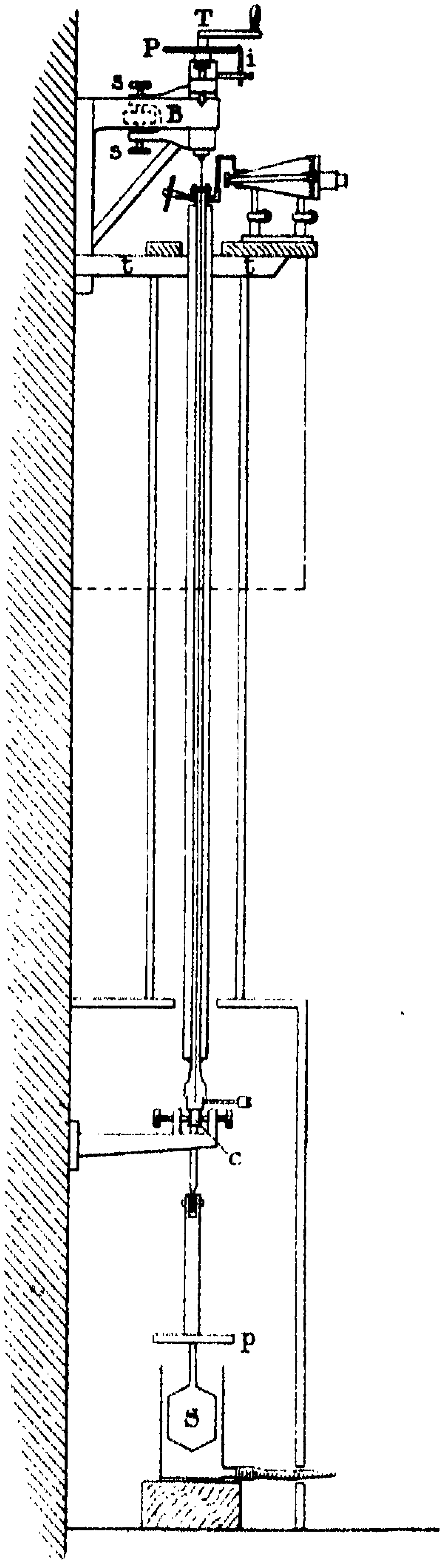

Fig. 1.

on a platform built up about 1·5 metres from the floor. The brass wire tube had an internal diameter about 2 mm. The top of the tube was fixed in a horizontal brass plate, in which was a hole about 0·25 mm. wider than the wire. On this plate rested a well-vaselined leather washer about 1·5 mm. thick, drilled so that it was fairly tight round the wire. On the washer was another brass plate, with a hole in it about 0·35 mm. wider than the wire. Four screws passed freely through holes in this upper plate, and were screwed into the lower plate. Springs between the heads of the screws and the upper surface of the upper plate gave sufficient pressure on the washer. It was found necessary to have the holes in the plates somewhat larger than the wire, in order to adjust the wire and the wire tube both vertical. An arm, not shown in fig. 1, projecting from the lower part of the apparatus, with a sliding weight on it in the plane of the upper side tubes, sufficed to make this vertical adjustment. At first I tried india-rubber washers. They were quite good when first put in, but they deteriorated rather rapidly, and, when they began to perish, they let a small quantity of water out of the tube when the wire moved. The leather washer only required renewal once, when it began to let water escape, and then, on examination, it appeared to be due to action on the wire, which was perceptibly rough on the surface where it emerged from the tube. A short length was cut off the lower end of the wire, and an equal length was let down through the upper chuck, so that once more a smooth part of the wire passed through the washer. There was no further difficulty, and no evidence again of any escape of water.

At the upper end of the wire tube there were two side tubes. A glass capillary tube was cemented into one, and bent as shown on the right in the figure, the vertical branch being about 10 cm. long. When the tube was filled with water, the level in the capillary was adjusted at the level of the microscope about 7 cm. above the level of the washer, as this was about the rise of water in the capillary due to surface tension, and there would therefore be no hydrostatic pressure on the water at the washer level. The tendency to leak would thereby be lessened, but the precaution was probably needless. Into the tube on the left a plunger passed through a leather stuffing box. The plunger had a diameter of 0·2060 cm., and it was driven to or fro by a micrometer screw of ½ mm. pitch. On the head of this screw was a 10 cm. plate, with 500 divisions on its circumference. This plunger was used ordinarily to adjust the level of the water in the capillary. But it was also used to calibrate the capillary. For this calibration, the usual observing microscope was replaced by a microscope cathetometer, and the change of water-level in the capillary was measured for one turn in or one turn out of the screw. Turning always in or always out, it was hardly possible to hit exactly on a whole turn, but a correction could be made, of course, for the fraction of a division in the micrometer head in excess or defect of a whole turn. The mean of 10 measurements when the micrometer was driven inwards 0·5 mm. gave a rise of 11·135 mm., with a range of 0·155 mm. between greatest and least. The mean of 10 measurements when the micrometer was drawn out 0·5 mm. gave a fall of 11·190 mm., with a range of 0·045 mm. The value was taken as 11·16 mm. This gives the cross-section of the capillary as 0·001493 sq. cm., and its diameter as 0·0436 cm.

At the lower end the wire tube was soldered on to a screw cap which could be screwed over the chuck gripping the lower end of the wire.

Below the chuck was a side tube used to fill the wire tube with water. For this purpose the side tube was connected with a flask in which water was boiled. The steam passed up through the crevices in the chuck and out at the plunger tube, from which the plunger was removed. A funnel containing water was connected on to the plunger tube, and when the water in this was boiling freely, through the passage of the steam, the flask was allowed to cool and water was sucked back into the wire tube. When it was full the flask was detached and a cap was screwed on to the lower tube. The plunger was replaced and the capillary, which had been closed meanwhile, was opened. By driving in the plunger the water was raised up to the level of the washer and to any desired point in the capillary.

When the apparatus was not being used the open end of the capillary was under water in a beaker, the plunger being driven in so that the capillary was entirely filled with water. The apparatus thus remained full of water whatever change of temperature might occur. When required for work the beaker was withdrawn and the plunger was screwed out till the meniscus was in the field of view of the microscope.

The wire tube was surrounded by an outer tube about 2·5 cm. diameter, filled with water. This merely served as a means of reducing the effect of outside or inside temperature changes. A wood casing covered with tin foil surrounded the whole from the floor up to the table to lengthen out still further any effects due to temperature change.

To observe the changes of level due to twisting, a microscope with a 1-inch objective and provided with a parallel plate micrometer was used. The micrometer scale was calibrated by means of a millimetre divided to tenths on a standard invar bar. Twelve determinations of 0·4 mm. gave 107·2 micrometer divisions equal to 1 mm., the determinations falling within about 1 per cent. range. Then 1 micrometer division = 0·00933 mm. Since the cross-section of the capillary is 0·001493 sq. cm., one division of the micrometer signifies a change of volume of the water in the wire tube of $1\cdot393 \times 10^{-6}$ c.c.

When it was desired to read the height of the water in the tube the micrometer plate was moved till the cross-wire in the microscope just touched the image of the lowest point of the capillary meniscus. The field was well illuminated by a small lamp behind the capillary, but the image was not always very distinct, and settings of the micrometer could not be trusted to, I think, two or three tenths of a division in some cases, though usually they were more exact. Close to the tube and between it and the micrometer plate a small vertical plate of glass was fixed to the tube at 45° to the line of sight, and this reflected the point of a needle which was also fixed to the tube, so that its image was in the same plane as, and close to, the image of the meniscus. This enabled the observer to note the position of either the meniscus or the needle point without moving the microscope.

When the wire lengthened the wire tube was let down by an equal amount, and the needle point fell. Let us call this fall NP.

At the same time the wire contracted laterally, and the meniscus fell in the tube, and the fall relative to the tube gave the change in volume. The fall observed was that relative to the tube plus that of the tube or NP.

Hence, if the fall observed in the microscope is T the fall relative to the tube is T − NP.

The Wires and their Preparation.

Two piano-steel wires were used in the experiments here described, No. I with a mean diameter 0·0986 cm., the diameters in two planes at right angles being measured with a micrometer every decimetre of its length. The measurements ranged from 0·980 to 0·989 at different points. No. II had a mean diameter of 0·1210 cm., measured in the same way, with a range at different points from 0·1207 to 0·1212.

It was found necessary to straighten these wires, for, unstraightened, they showed the effect with light loads noticed in the previous paper, an apparent shortening on twisting, due, I think, to coiling. To straighten them they were loaded and an electric current was passed through them. No. I was loaded with 50 kgrm., and received a current of 10 ampères. No. II was loaded with 60 kgrm., and received a current of 16 ampères. In each case the wire drew out slightly and then stopped, acquiring a blue temper without rising to a red heat.

Of course the wires became circularly magnetised, but the magnetisation can hardly have contributed to the results here to be described, as these results are of the same character and order as results obtained with heavily loaded unannealed wires in a number of preliminary experiments made before the experiments took their final shape.

A few experiments were made on a hard drawn copper wire, mean diameter 0·1219 cm. (with a range from 0·1216 to 0·1224 cm.).

The Method of Measuring the Lowering on Twisting.

In making any determination of NP or T the following plan was adopted. Suppose, for instance, that the value of T was to be found for four turns of the wire clockwise as seen from above. The position of the meniscus was read for no twist at a given minute, then my assistant put on four turns clockwise—denoted by C_4—then he gave a signal just before, and again exactly at the next half minute, and I set the cross wire on the meniscus at the half minute. The micrometer was read, and the twist was taken off. At the next half minute the micrometer was set as before. Again C_4 was put on, and so on, usually for 32 observations. The first two or three readings were not taken into account, as initially there was usually some irregularity, due probably to settling down in the bearing. The readings were combined in threes in the usual way to give $T = \frac{1}{2}(a+c)-b$ to eliminate as far as possible any march of the zero reading. With the meniscus there was almost always a march, due chiefly to temperature change, for, of course, the arrangement was a very sensitive thermometer. The mean result of the 32 observations was equivalent to 15 or 16 independent determinations. To determine NP the same course was followed, except that the time was not noted. For, though there was often a march in the zero, it was very much smaller, and the observations were made at sufficiently nearly equal intervals of time without noting exact times. This small march was doubtless partly due to temperature change, but also partly due, I believe, to further settling down of the cone of the twisting head into its bearing through slow squeezing out of the oil. In reconstruction I should try the effect of replacing the conical bearing by a ball bearing.

Before the reading was made it was found to be absolutely necessary to move the head-piece some ten or fifteen times to and fro through a small angle—perhaps diminishing from 20°—on each side of the final position. If this was not done the wire did not sink down or rise up to its final position, probably owing to some small friction in the leather washer. After the alternating motion of the head-piece had been given ten or fifteen times no further alternation made any difference in the reading. It was only after finding the necessity of this that I obtained consistent readings.

The maximum and minimum values of NP in a set of 30 determinations usually differed by about 0·4 division, only once rising to 0·8 division.

The maximum and minimum values of T in a set of 30 differed more, as might be expected; the difference averaging 1·7 divisions, and once rising to nearly 5 divisions. This, however, was in the case of the least load, when the weight was probably insufficient to keep the wire tube quite vertical.

Subsidiary Experiments.

The three following subsidiary experiments were made in order to justify the methods of measuring the changes of dimensions on twisting:—

1. To show that the lengthening on twisting is not due to a change in Young's modulus, Y.

This is satisfactorily proved by the experiments on twisting described below. For, suppose that we have a stress P applied to the end of the wire by a load stretching length l by dl when the wire is not twisted, we have $dl = \mathrm{P}l/\mathrm{Y}$. Now let the wire thus loaded be twisted through, say, four turns and let the lowering through twisting be δ. If this is due to a change in Young's modulus to Y', $dl+\delta = \mathrm{P}l/\mathrm{Y}'$. Whence $\delta = \mathrm{P}l(\mathrm{Y}'^{-1}-\mathrm{Y}^{-1})$, and δ should be proportional to P, whereas it is found to be very nearly the same for loads varying from 5 to 50 kgrm. (approximately).

It appeared worth while, however, to test the question directly, by finding the extension of wire 1 for very different loads when 1·02 kgrm. was added, first with the wire untwisted, then with the wire twisted through four turns clockwise. The following results, in micrometer divisions, were obtained, each the mean of a number of measurements:—

Table I.

Load.	No twist. Lowering for 1·02 kgrm.	$\dot{C}_4$ twist. Lowering for 1·02 kgrm.
18·5	10·56	10·52
38·5	10·68	10·80
48·5	10·50	10·82
Means	10·58	10·57

Then a twist of four turns produced no measurable change in Young's modulus.

2. To show that the rise and fall of the liquid meniscus were due to, and measured, the change in volume of the wire in the wire tube.

The most satisfactory way of showing this appeared to consist in using the apparatus to measure Poisson's ratio σ. The load was altered by 1·02 kgrm. by alternately immersing the sinker in water and letting the water run out.

The rise and fall of the needle point gave the end extension, and Young's modulus Y could then be calculated; while the rise and fall of the meniscus gave the volume change, and the side contraction and Poisson's ratio σ could be calculated. The rigidity modulus n could be obtained from $n = \frac{1}{2}Y/(1+\sigma)$.

When the load was increased there was some yield of the supporting bracket. To determine its amount, a needle point was fixed on the bracket close to the upper chuck and sighted by the microscope. A series of loads up to 50 kgrm. showed that the lowering per kilogramme was 0·06 division. An addition of 1·02 kgrm., therefore, lowered the bracket by 0·061 division, and this had to be subtracted from the NP reading when used to find Y. In the lowering of the meniscus T−NP, it obviously did not come into consideration. The observed change of volume given by T−NP had to be corrected by a factor about 160·5/156, since only 156 cm. of wire were within the wire tube and 4·5 cm. were outside. The actual length outside varied from 4·2 to 4·6, and the factor was varied accordingly.

No doubt better values of Y and σ might have been obtained with a larger change of load, but, to test the apparatus, it was important to observe lowerings of the same order as those observed in the twisting. In the following Table II the values of T−NP and NP, due to an addition of 1·02 kgrm., are given in micrometer divisions corrected as above described. Each value is the mean of 30. The range between maximum and minimum in a set averaged 1·7 division for T and 0·57 division for NP:—

Table II.—Elastic Moduli and Poisson's Ratio.

Load in kgrm.	NP.	T−NP.	σ.	10^{-12} Y.	10^{-12} n.
		Steel Wire I, Diameter 0·0986 cm.			
18·5	10·65	29·86	0·272	2·11	0·830
28·5	10·60	29·57	0·271	2·12	0·835
38·5	10·74	29·37	0·265	2·09	0·828
48·5	10·44	29·05	0·270	2·16	0·849
Mean values...	—	—	0·270	2·12	0·835
		Same Wire with C_4 Twist on it.			
48·5	10·27	28·04	0·265	2·18	0·861
		Steel Wire II, Diameter 0·1210 cm.			
48·5	7·05	31·22	0·287	2·12	0·825
		Hard-drawn Copper Wire, Diameter 0·1219 cm.			
18·5	11·20	61·52	0·331	1·31	0·493

The values found for a steel wire after annealing, given in the paper already referred to,[*] were $Y = 2{\cdot}06 \times 10^{12}$, $n = 0{\cdot}809 \times 10^{12}$ (by vibration), whence $\sigma = 0{\cdot}273$.

The values for the steel wires are sufficiently near to each other and to the values previously found to show that the tube readings gave, at any rate, very nearly the true changes in volume.

3. To show that the changes were very nearly isothermal.

The change in temperature of a solid sheared adiabatically through ϵ is—

$$d\theta = -\lambda n\theta\epsilon^2/2JC_p\rho,$$

where λn is the decrease in rigidity per degree rise, θ is the absolute temperature, C_p is the specific heat, and ρ is the density.

Let us suppose that a steel wire 156 cm. long and 0·05 cm. radius—nearly wire I—is twisted through one turn. It is sufficient to investigate the effect for one turn, for both the adiabatic temperature change and the twisting effects are proportional to the square of the shear, and therefore in a ratio independent of the shear. Then $\epsilon = 2\pi r/156$, where r is the distance of an element from the axis. The mean change in temperature of such a wire is

$$\int_0^a \frac{2\pi r\, d\theta\, dr}{\pi a^2} = -\frac{\pi^2 a^2 \lambda n\theta}{JC_p\rho 156^2},$$

where $a = 0{\cdot}05$.

For steel we may put $n = 10^{12}$, $\lambda = 2 \times 10^{-4}$, $\rho = 7{\cdot}8$, $C_p = 0{\cdot}112$. Taking θ as 300° A. we find the heat in calories developed by the twist to be about -18×10^{-4} calories. Or on untwisting $+18 \times 10^{-4}$ calories.

If this heat were confined to the steel it would alter its temperature by about 1/600° C. and its linear dimensions by about $1{\cdot}8 \times 10^{-8}$ in 1. The twisting through one turn, as will be seen below, alters the radius by about $3{\cdot}19 \times 10^{-7}$ in 1 and the length by about $1{\cdot}72 \times 10^{-6}$. The effects of an adiabatic change of temperature would, therefore, be appreciable compared with the effects of twisting, especially on the radius. But the wire shares its heat, positive or negative, with the water in the wire tube, and here it may produce a serious effect, if it gets no farther than the wire tube, owing to the considerable coefficient of expansion of the water. Let us suppose that the heat or cold is shared with the water in the wire tube so rapidly that both are at one temperature. The water, having approximately three times the volume of the steel, has about 7/9 the heat capacity of steel plus water. So that the water would receive about 14×10^{-4} calories. If a mass of water at a temperature at which its cubical expansion is α receives H calories its change of volume is Hα, whatever the total volume. In our case the temperature was usually about 12° C., at which α is about 10^{-4}. Then the volume change would be about 14×10^{-8} c.c. and since one micrometer division is about 14×10^{-7} c.c. along the capillary, one turn, through thermal effect alone, would produce a fall on twisting and a rise on untwisting of about 0·1 division. The actual change observed on twisting through one turn was about 0·56 division. If then the heat or cold only slowly spread from the wire, or again if it were rapidly shared with the water in the wire tube but only slowly spread thence, the measurements would be seriously affected. But it is obvious that there must, in reality, be a rapid adjustment of temperature between the wire tube and the outer water jacket, and it was important to find out how rapidly the adjustment progressed. Fortunately the wire was insulated from the tube where it passed through the washer, so that it was easy to pass an electric current through it by connecting the terminals of a battery, one to the bracket, the other to the wire tube. Heating currents of the order of 1 to 2 ampères were thus passed along the wire. The current was put on for 2 seconds, the meniscus rushing up meanwhile fairly uniformly, and the point to which it rose was read on the micrometer. Then, 15 seconds after the cut off, the position of the meniscus was read again and the mean of a number of determinations showed that after 15 seconds only 0·032 of the original rise remained. The original rise varied from 7 to 18 divisions with different currents. If the twisting were made instantaneously and the reading of the fall in the tube were made 15 seconds later, about $0{\cdot}032 \times 0{\cdot}1 \div 0{\cdot}56 = 0{\cdot}006$ of the fall would be due to the cooling on twisting. But this is a very considerable over-estimate. The twisting was usually begun 25 seconds before reading and ended more than 15 seconds before. The effect of temperature change may, I think, be estimated at less than 1/300 of the whole. It was impossible to assign even an approximate value to it and as it proved to be so small it was neglected. The effect would have been reduced altogether beyond consideration if the readings had been taken at intervals of one minute, but this would have introduced errors, probably much worse, through irregularities in the temperature march.

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[*] *Loc. cit.*, p. 554.

In the experiments on Poisson's ratio the adiabatic change of temperature on adding a load which stretches length l by dl is

$$d\theta = -\alpha Y \theta dl / J C_p \rho l,$$

where αY is the change in Young's modulus per degree. The value of α for steel is about 1/4000. This gives the heat for a stretch of 10 divisions as about -9×10^{-8} calories. With uniform temperature of steel and water in the wire tube the water would have about 7×10^{-3} calories, and its effect would be about 0·5 division. After 15 seconds it would be about 0·016 division. As the change of level observed was about 30 divisions the effect is negligible. The direct effect in lengthening or shortening the wire is easily shown to be very much smaller.

Measurement of the Changes of Dimensions on Twisting.

The method of making the measurements has been described already. In the case of Wire I, NP, or the lengthening of the wire, was observed for various loads for four turns and for two turns clockwise twist, denoted by C_4 and C_2, and for four turns and for two turns counter-clockwise twist, denoted by CC_4 and CC_2, each value being the mean of 30 determinations—once or twice of 40—made as described above. As permanent set came in with five turns, four turns was the maximum twist employed. The mean values of T were also determined for the same four twists and T − NP was corrected for the length of wire outside the wire tube. For one load on Wire I the lowerings for C_3 and CC_3 were also observed.

In all cases the lowering w could be represented very nearly by the parabola

$$L(n+c)^2 = w+b,$$

where n is the number of turns put on and L, c, and b are constants, not, of course, the same for NP and T − NP. The constant c represents the fraction of a turn always on the counter-clockwise side of the point of no twist, about which the lowering is symmetrical. Putting $n = -c$, $b = -w$ is a small shortening, or for a counter-clockwise twist c the wire has a minimum length. The existence of c and b is due to want of homogeneity in the wire. They may be explained by supposing that the wire consists of a core and a sheath twisted against each other in the apparently neutral condition as will be shown in the theory given later. Owing to want of exact centering the image "wobbled" somewhat in the field during twisting, and only returned to the same vertical line after a whole number of turns, so that it was futile to attempt to measure b. But there was fairly conclusive evidence that it had a real existence.

According to the theory given, L is the all-important quantity. The internal strain only shifts the vertex of the parabola without altering its size.

To find the constants of a parabola which should fairly represent the results, it was assumed that the curve went through the point $w = 0, n = 0$, so that $Lc^2 = b$.

The equation then becomes

$$L(n^2+2nc) = w.$$

Let w be the lowering for C_n, and w' that for CC_n, then

$$L(n^2-2nc) = w',$$

whence

$$L = (w+w')/2n^2 \quad \text{and} \quad c = (w-w')/4nL = \tfrac{1}{2}n(w-w')/(w+w').$$

The errors are given by

$$\delta L = \delta(w+w')/2n^2, \quad \text{and} \quad \delta c = \delta(w-w')/4nL,$$

assuming that L is without error in c.

If then we find the value of L, say L_4, from the lowerings at C_4 and CC_4, and the value of L, say L_2, from those at C_2 and CC_2, the value of the former should have four times the weight of the latter and we may take the best value of L as $\frac{1}{5}(4L_4 + L_2)$.

The value of c determined from C_4 and CC_4 should have twice the weight of that determined from C_2 and CC_2, and we may take the best value as $\frac{1}{3}(2c_4 + c_2)$.

In the following tables the results are set out. In Table III the lengthening of the wire I is given in micrometer divisions, and below each lengthening the difference, calculated − observed, is put in italics, the calculated values being those given by the parabolas of which the constants are given in Table IV. Similar tables are given for wire II, and for the hard drawn copper wire, but for a single load only, sufficient to secure good centering. After the experience with various loads with wire I, it appeared unnecessary to vary the load in the other cases. With wire II it was not thought advisable to go beyond three turns, and with the copper wire beyond one turn owing to permanent set, which began to be very considerable beyond those limits. The mode of calculating the best parabola was modified accordingly.

Table III.—Lowering NP for Steel Wire I, diameter 0·0986 cm.

Load.	C_4.	C_2.	O.	CC_2.	CC_4.
kgrm.					
48·5	5·095	1·452	0	0·768	4·233
	+0·06	*−0·03*	*0*	*+0·13*	*−0·13*
38·5	5·358	1·422	0	0·818	4·152
	−0·05	*+0·06*	*0*	*+0·06*	*−0·05*
28·5	5·265	1·500	0	0·858	4·259
	+0·01	*+0·03*	*0*	*+0·04*	*−0·10*
18·5	5·382	1·680	0	0·905	4·091
	+0·14	*−0·13*	*0*	*−0·04*	*+0·06*
4·7	5·407	1·742	0	0·797	3·865
	+0·13	*−0·15*	*0*	*−0·03*	*+0·04*

For load 28·5 C_3 was 3·048, and CC_3 was 2·187, and these were taken into account in calculating the parabola, the differences in each case being *+0·05*.

Table IV.—Constants of Parabolas for Table III.

Load.	L.	c.	b.
48·5	0·289	0·226	0·015
38·5	0·294	0·256	0·019
28·5	0·295	0·287	0·017
18·5	0·302	0·281	0·024
4·7	0·295	0·345	0·035

There was probably some permanent set given in the last two owing to accidental over-twisting of the wire.

The mean value of L is 0·295, and within errors of observation it is independent of the load. It is hardly likely that this is strictly true.

Table V.—Lowering of the Meniscus T—NP for Wire I corrected for length Outside the Tube.

Load.	C_1.	C_2.	O.	CC_2.	CC_4.
48·5	11·69	3·94	0	0·07	6·65
	+0·33	*−0·17*	*0*	*+0·63*	*−0·78*
38·5	11·63	3·94	0	0·84	6·36
	+0·22	*−0·28*	*0*	*+0·06*	*−0·22*
28·5	11·82	4·00	0	1·18	6·38
	−0·25	*−0·28*	*0*	*−0·23*	*+0·04*
18·5	10·99	2·84	0	1·00	6·17
	+0·36	*+0·37*	*0*	*−0·02*	*−0·02*
4·7	10·17	2·54	0	0·99	8·24
	−0·14	*+0·30*	*0*	*+0·57*	*−0·72*

For load 28·5 C_3 was 7·33 and CC_3 was 2·86. These were used in calculating the parabola, and the differences were respectively *−0·01* and *+0·23*.

Table VI.—Constants of Parabolas for Table V.

Load.	L.	c.	b.
48·5	0·559	0·60	0·26
38·5	0·569	0·61	0·21
28·5	0·578	0·61	0·21
18·5	0·525	0·54	0·15
4·7	0·548	0·29	0·05

As the errors of observation with the last two loads were about double those for the earlier loads, they are only given half the weight in finding L. The value of L is taken as 0·561.

Table VII.—Lowering NP for Steel Wire II, Diameter 0·1210 cm.
Two Independent Sets.

	Load.	C_3.	C_2.	O.	CC_2.	CC_3.
I.	48·5	4·922 *+0·05*	2·368 *−0·06*	0 *0*	1·740 *−0·04*	4·000 *+0·05*
II.	48·5	4·983 *−0·06*	2·243 *+0·05*	0 *0*	1·708 *−0·01*	4·049 *0·00*

Table VIII.—Constants of Parabolas for Table VII.

	L.	*c*.	*b*.
I	0·501	0·154	0·012
II	0·499	0·147	0·011

The mean value of L is 0·500.

Table IX.—Lowering of the Meniscus T—NP for Wire II, Corrected for length outside the Tube.

	Load.	C_3.	C_2.	O.	CC_2.	CC_3.
I.	48·5	15·16 *+0·20*	7·73 *−0·25*	0 *0*	3·90 *−0·31*	9·22 *+0·33*
II.	48·5	15·48 *+0·04*	7·61 *−0·06*	0 *0*	3·71 *−0·07*	9·55 *+0·10*

Table X.—Constants of Parabolas for Table IX.

	L.	*c*.	*b*.
I	1·385	0·35	0·17
II	1·398	0·35	0·17

The mean value of L is 1·392.

Copper Wire. Diameter, 0·1219 cm.

I was only able to use C_1 and CC_1 owing to permanent set.

The values of NP were 1·043 and 0·415, and the parabola going through these points and the origin is $0·73\,(n+0·22)^2 = w+0·03$.

The values of T − NP, corrected for 4·2 cm. outside the tube, were 8·007 and 1·433, and the parabola is $4{\cdot}72\,(n+0{\cdot}35)^2 = w+0{\cdot}58$.

The work given in the former paper appears to justify the assumption of the parabolic law for copper.

The End Elongation, Side Contraction, and Volume Increase.

Steel Wire I. Diameter, 0·0986 cm.

If w is the end lowering for one turn from the position of minimum length assumed to be L divisions,

$$w = \text{L} \times \text{length of one micrometer division}$$
$$= 0{\cdot}295 \times 933 \times 10^{-6} = 2{\cdot}75 \times 10^{-4} \text{ cm.}$$

The length is $l = 160{\cdot}5$. Then

$$w/l = 1{\cdot}71 \times 10^{-6}.$$

If u is the decrease in the radius a for one turn,

$$2\pi aul = \text{L} \times \text{volume of one micrometer division of capillary,}$$
$$u = 0{\cdot}561 \times 1{\cdot}393 \times 10^{-6}/2\pi \times 0{\cdot}0493 \times 160{\cdot}5$$
$$= 1{\cdot}57 \times 10^{-8} \text{ cm.}$$

The radius is 0·0493 cm. Then

$$u/a = 3{\cdot}19 \times 10^{-7}.$$

The ratio side contraction/end elongation, namely,

$$u/a \div w/l = 0{\cdot}187.$$

If dv is the volume increase in total volume v,

$$dv/v = (\pi a^2 w - 2\pi alu)/\pi a^2 l$$
$$= w/l - 2u/a = 1{\cdot}07 \times 10^{-6}.$$

All the quantities w/l, u/a, dv/v are proportional to the square of the twist from the point of minimum length. The ratio $u/a \div w/l$ is the same for all twists.

Steel Wire II. Diameter, 0·1210 cm.

Using the values given in the tables, we have for one turn—

$$w = 4{\cdot}66 \times 10^{-4} \text{ cm.,} \qquad u/a = 5{\cdot}24 \times 10^{-7},$$
$$w/l = 2{\cdot}90 \times 10^{-6}, \qquad u/a \div w/l = 0{\cdot}181,$$
$$u = 3{\cdot}17 \times 10^{-8} \text{ cm.,} \qquad dv/v = 1{\cdot}85 \times 10^{-6}.$$

Copper Wire. Diameter, 0·1219 cm.

The corresponding quantities given by the single set of observations are not of such weight as those for Wires I and II, but I add them here—

$$w = 6{\cdot}81 \times 10^{-4} \text{ cm.}, \qquad u/a = 1{\cdot}75 \times 10^{-6},$$
$$w/l = 4{\cdot}25 \times 10^{-6}, \qquad u/a \div w/l = 0{\cdot}41,$$
$$u = 10{\cdot}7 \times 10^{-8} \text{ cm.}, \qquad dv/v = 0{\cdot}75 \times 10^{-6}.$$

On comparing the results for Wires I and II we see that side contraction ÷ end elongation is very nearly the same for both. The theory given below makes both w/l and u/a proportional to the square of the radius for wires of the same material undergoing the same twist. But as far as these two wires are concerned they are very nearly proportional to $(\text{radius})^{2{\cdot}5}$. I do not think the discrepancy is to be ascribed to experimental error. Perhaps the theory is inadequate, but I think that it is more probable that slight differences in the material not greatly affecting the ordinary elastic moduli may produce very considerable changes in what we may term the secondary moduli, which, in the theory below, are denoted by p and q.

I should like to have taken observations on several more steel wires with a wider range of diameters, but I am not able to continue the work at present.

Experimental Verification of a Reciprocal Relation.

In the 'Philosophical Magazine' for November, 1911, vol. 22, p. 740, Dr. R. A. Houstoun has expressed the reciprocal relation between the stretching and twisting of a wire (confined within limits of reversibility) in the form

$$\left(\frac{d\theta}{dF}\right)_{G \text{ const.}} = \left(\frac{dw}{dG}\right)_{F \text{ const.}}, \tag{1}$$

where F is the end pull and w the increase in length, G the torque, and θ the twist on the wire (I use letters for length and torque differing from Dr. Houstoun's).

As the apparatus only needed small modification it appeared to be worth while to see how nearly this relation was verified, and Wire II was used for the purpose. Incidentally, the value of the rigidity was obtained by the statical torque method.

When the observations needed are worked out it is found that they are identical, as of course was to be expected, with those needed to verify the relation

$$\left(\frac{dF}{d\theta}\right)_{w \text{ const.}} = \left(\frac{dG}{dw}\right)_{\theta \text{ const.}}, \tag{2}$$

which is the more direct expression of the Conservation of Energy in these phenomena.

Taking equation (1) we require to know on the left the extra twist $d\theta$ which must be put upon the wire to keep G the same when a load dF is added. For this purpose the wire was initially loaded with 18·5 kgrm., and the head was turned through a right angle. The bar at the bottom was also turned through a right angle from its usual position. On the cross-bar a mirror was fixed reflecting into a telescope a millimetre scale 156·5 cm. away. The ends of the cross-bar were rounded into arcs of a circle with centre in the axis of the wire and radius 14·70 cm. Horizontal threads passed off these arcs to two very light horizontal spiral springs which stretched very uniformly in proportion to the pull up to 40 or 50 grm. These springs were attached to the bases of two travelling microscopes, of which the horizontal scales merely were used to measure any change in stretch. Initially, the wire was without twist, and the position of the cross-bar on the scale was read. It would have been at least very difficult to determine directly the total stretch of the springs required to keep the cross-bar in position when the head was twisted, so the following plan was adopted :—

A half-turn CC was put on by the head-piece, and the springs were stretched so as to bring the cross-bar to its original position. Then a further turn and a half CC was put on, and the *additional* stretch of each spring needed to keep the cross-bar in position was read. This additional stretch multiplied by 4/3 gave the total stretch of the springs, and thus the pull exerted at each end of the cross-arm needed to maintain two turns twist on the wire. The full stretches thus computed were 12·340 cm. on the left and 12·384 cm. on the right, corresponding to pulls, according to previous calibration, of 49·24 grm. and 46·87 grm., mean 48·06 grm. The torque was therefore

$$G = 48{\cdot}06 \times 981 \times 29{\cdot}4 = 1{\cdot}38 \times 10^6 \text{ cm. dynes.}$$

From this the rigidity is

$$n = 0{\cdot}838 \times 10^{12}.$$

The tube method gave $0{\cdot}825 \times 10^{12}$, and the nearness of the two values appears to show that the springs could be trusted fairly well.

A load $dF = 30$ kgrm. was then added, and the torque for two turns was thereby diminished. The springs therefore contracted, and it was observed that they pulled the cross-bar round through 15·85 mm. on the scale—the mean of five different observations ranging from 15·45 to 16·55, or through an angle 0·00507 radian.

Denoting this angle by $\delta\theta$, and the radius of the cross-bar arm by b, and the decrease of torque by δG

$$\frac{\delta G}{G} = \frac{b\delta\theta}{s}, \tag{3}$$

where s is the whole mean stretch of the springs for two turns.

But we require the twist $d\theta$, which must be put on the wire from its initial two turns, and in the opposite direction from $\delta\theta$, to restore the torque to G. This is given by

$$\frac{G}{G-\delta G} = \frac{\theta+d\theta}{\theta-\delta\theta}, \quad \text{where } \theta = 4\pi,$$

whence, on substituting for $\delta G/G$ from (3), we get

$$d\theta = \left(\frac{b\theta}{s}-1\right)\delta\theta, \quad \text{and} \quad \frac{d\theta}{dF} = \left(\frac{b\theta}{s}-1\right)\frac{\delta\theta}{dF}. \tag{4}$$

Taking the right hand of equation (1), we require to know the lowering dw for a change dG in the torque under constant load. We get the lowering from the equation

$$L(n-c)^2 = w+b,$$

giving

$$dw = 2L(n-c)\,dn = L(n-c)\frac{d\theta}{\pi}.$$

Also

$$dG = \frac{G\,d\theta}{\theta}.$$

Then

$$\frac{dw}{dG} = \frac{L(n-c)\,\theta}{\pi G}. \tag{5}$$

Equating (4) and (5), we ought to find

$$L = \frac{\pi G}{n-c}\left(\frac{b\theta}{s}-1\right)\frac{\delta\theta}{\theta\,dF}. \tag{6}$$

Substituting the known values on the right, viz., $G = 1{\cdot}38\times 10^6$, $n = 2$, $c = 0{\cdot}15$, $b = 14{\cdot}7$, $\theta = 4\pi$, $s = 12{\cdot}37$, $\delta\theta = 0{\cdot}00507$, $dF = 30\times 981000$, we get

$$L = 4{\cdot}48\times 10^{-4}.$$

The observed value of L is given as w on p. 548, viz.,

$$L = 4{\cdot}66\times 10^{-4},$$

showing as close an agreement as could be expected, considering the errors of observation.

Taking the second reciprocal relation (2), to find $\left(\frac{dF}{d\theta}\right)_{w\ \text{const.}}$ we must twist through $d\theta$ and observe dw, and then calculate what load dF must be removed to restore the original length.

We have $\quad dw = L(n-c)\dfrac{d\theta}{\pi}, \quad$ and $\quad dF = \pi a^2 Y\,dw/l.$

Then

$$\frac{dF}{d\theta} = \frac{L(n-c)\,a^2 Y}{l}. \tag{7}$$

To find $\left(\frac{dG}{dw}\right)_{\theta\text{ const.}}$, we put on a load W and observe $\delta\theta$. If δG is the diminution in torque at this point and dG the diminution in torque with the original twist θ,

$$\frac{G-\delta G}{G-dG}=\frac{\theta-\delta\theta}{\theta}.$$

Substituting for $\delta G/G$ from (3), this gives

$$dG=\left(\frac{b\theta}{s}-1\right)\frac{G\delta\theta}{\theta},$$

the change in torque for addition W when θ is constant.

The value of dw for this load is

$$dw = lW/\pi a^2Y,$$

and

$$\left(\frac{dG}{dw}\right)_{\theta\text{ const.}}=\left(\frac{b\theta}{s}-1\right)\frac{\pi a^2YG}{lW\theta}\delta\theta. \tag{8}$$

Equating (7) and (8) and putting dF for W, we get

$$L=\frac{\pi G}{n-c}\left(\frac{b\theta}{s}-1\right)\frac{\delta\theta}{\theta dF},$$

the same equation as before.

If we could use a wire without any internal strain when untwisted, c would be zero, and we could calculate L, the lowering for one turn, from observations on the torque and load alone.

A Theory of the Changes of Dimension on Twisting: The Stresses in a Finite Pure Shear.

In the paper already referred to[*] I showed that in a finite pure shear ϵ such as is represented in fig. 2, in which a cube of section ABCD is sheared into a figure of section ABKL through an angle CBK = ϵ, the thicknesses perpendicular to AB and to the plane of the figure remaining constant, the lines of maximum elongation and contraction are, to the order of ϵ^2, at right angles before the shear, making $\epsilon/4$ with the diagonals of the square, as AE and BG. After the shear they are again at right angles to the order of ϵ^2, and make $\epsilon/4$ with the diagonals on the other side as AF and BH. Since we have elongation in one direction AF, and contraction in a direction BH at right angles, the shear may be maintained by a pressure P along BH and a tension Q along AF as far as forces in the plane of the figure are concerned.

If we go to the first order of ϵ only,

$$P = Q = n\epsilon.$$

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[*] *Loc. cit.*, p. 546.

If we go to the second order we must put

$$P = n\epsilon + p\epsilon^2,$$

where p is a constant to that order.

If we reverse ϵ, P becomes equal to $-Q$, so that we have

$$-Q = -n\epsilon + p\epsilon^2 \quad \text{or} \quad Q = n\epsilon - p\epsilon^2.$$

We can only assume that there is no pressure or tension perpendicular to the plane of the figure, if we neglect ϵ^2. Going to the second order, we have to allow the possibility of a pressure of that order, which we may put as

$$S = q\epsilon^2,$$

where if q is negative the force is a tension.

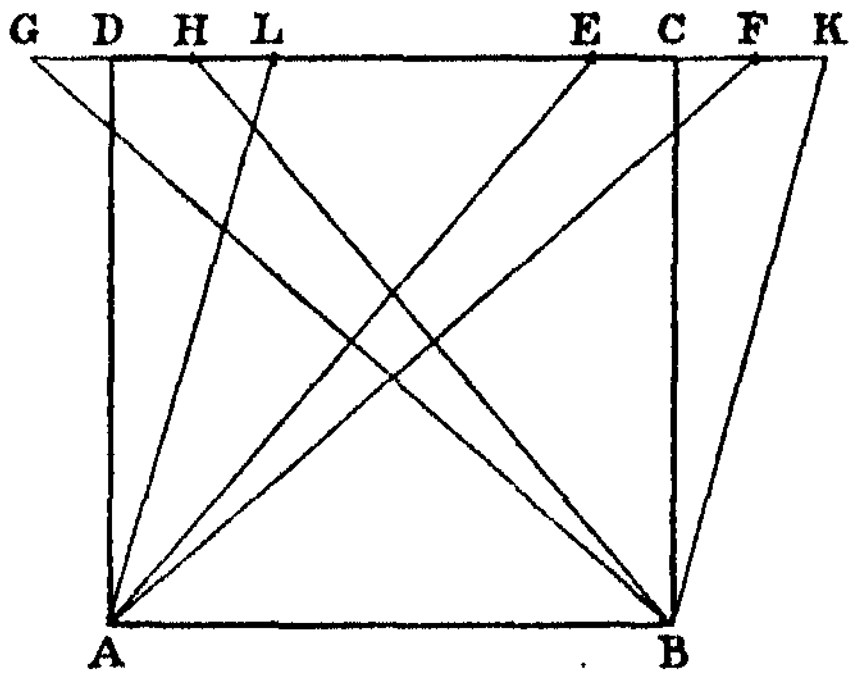

FIG. 2.

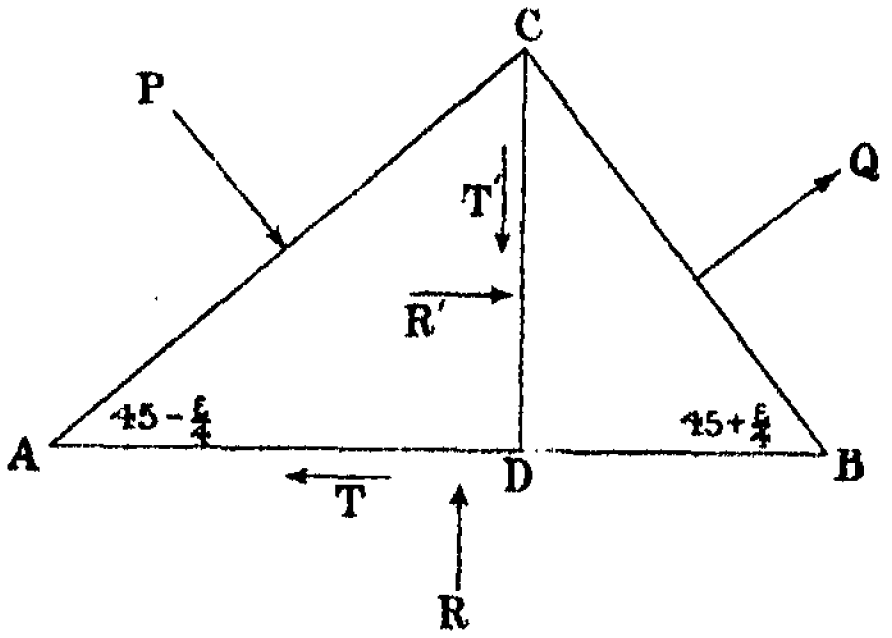

FIG. 3.

Considering the equilibrium of the wedge ABC, fig. 3, with AC in the direction of greatest elongation and BC in that of greatest contraction, I showed that the tangential stress along AB is, to the second order,

$$T = n\epsilon,$$

and that a pressure is required perpendicular to AB given by

$$R = (\tfrac{1}{2}n + p)\,\epsilon^2.$$

The analysis stopped here and was incomplete, as no account was taken of the stresses on the plane CD, fig. 3, perpendicular to AB. It requires to be supplemented as follows:—

Considering the equilibrium of the wedge CDB, let us suppose that on CD there is a tangential stress T′ along CD, and a pressure R′ perpendicular to it.

Resolving all the forces on CDB parallel to DB,

$$R'.\,CB\sin(45+\tfrac{1}{4}\epsilon) - T.\,CB\cos(45+\tfrac{1}{4}\epsilon) + Q.\,CB\sin(45+\tfrac{1}{4}\epsilon) = 0,$$

whence

$$R' = T\cot(45+\tfrac{1}{4}\epsilon) - Q;$$

or, since $T = n\epsilon$ and $\cot(45+\frac{1}{4}\epsilon) = (1-\frac{1}{2}\epsilon)$, neglecting ϵ^2, as it is multiplied by ϵ,

$$R' = n\epsilon(1-\tfrac{1}{2}\epsilon)-n\epsilon+p\epsilon^2 = (-\tfrac{1}{2}n+p)\,\epsilon^2.$$

Resolving parallel to CD,

$$T'.\,CB\sin(45+\tfrac{1}{4}\epsilon)-R\,.\,CB\cos(45+\tfrac{1}{4}\epsilon)-Q\,.\,CB\cos(45+\tfrac{1}{4}\epsilon) = 0,$$

whence
$$T' = (R+Q)\cot(45+\tfrac{1}{4}\epsilon) = \{(\tfrac{1}{2}n+p)\,\epsilon^2+n\epsilon-p\epsilon^2\}\,(1-\tfrac{1}{2}\epsilon)$$
$$= n\epsilon \text{ to the second order.}$$

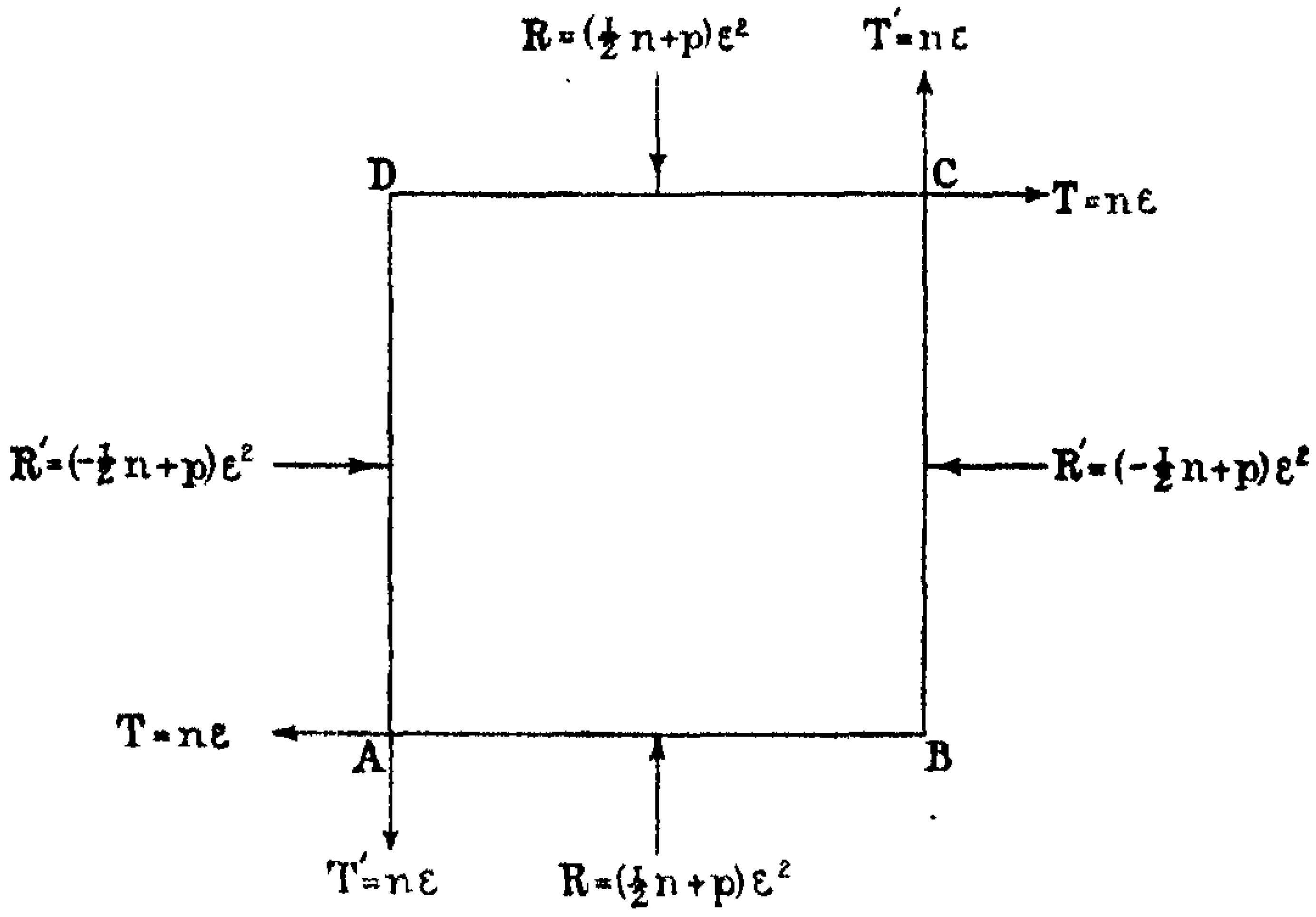

FIG. 4.

On a unit cube of the material in the sheared condition then, we have, as in fig. 4,

Tangential stresses along AB and CD each.........	$n\epsilon$.
Tangential stresses along AD and BC each.........	$n\epsilon$.
Pressures perpendicular to AB and CD each	$(\frac{1}{2}n+p)\,\epsilon^2$.
Pressures perpendicular to AD and BC each	$(-\frac{1}{2}n+p)\,\epsilon^2$.
And pressures perpendicular to the plane of the figure each $q\epsilon^2$, or, in more convenient form ...	$(q-p)\,\epsilon^2+p\epsilon^2$.

The Strains in a Finite Shear Stress consisting of Tangential Stress T, T′ *only*.

If an element is subjected to the system of stresses just investigated, when we put on to it a system of tensions equal and opposite to the second-order pressures we have just found, we leave only the tangential stresses $T = T' = n\epsilon$. The strains due to these tensions must be superposed on the shear ϵ, and we shall then have the strains due to the tangential stresses only.

We have then to examine the strains due to tensions—

$$(\tfrac{1}{2}n+p)\epsilon^2 \text{ on AB and CD (fig. 4).}$$
$$(-\tfrac{1}{2}n+p)\epsilon^2 \text{ on AD and BC.}$$
$$(q-p)\epsilon^2+p\epsilon^2 \text{ perpendicular to the plane of the figure.}$$

Through the tension $p\epsilon^2$ on every face we get an extension in all directions $p\epsilon^2/3\mathrm{K}$, where K is the bulk modulus.

The tensions $\frac{1}{2}n\epsilon^2$ on AB and CD and the pressures $\frac{1}{2}n\epsilon^2$ on AD and BC constitute a shear stress giving elongation parallel to BC $\frac{1}{4}n\epsilon^2/n = \frac{1}{4}\epsilon^2$, and a contraction parallel to AB also $\frac{1}{4}\epsilon^2$.

The tensions $(q-p)\epsilon^2$ perpendicular to the plane of the figure give an elongation perpendicular to that plane $\frac{1}{\mathrm{Y}}(q-p)\epsilon^2$, and contractions at right angles, viz., along AB and AD, $\frac{\sigma}{\mathrm{Y}}(q-p)\epsilon^2$, where Y is Young's modulus and σ is Poisson's ratio.

Collecting the results, we have secondary strains accompanying the shear ϵ as follows:—

An elongation parallel to BC $= \frac{1}{4}\epsilon^2+\frac{p\epsilon^2}{3\mathrm{K}}-\frac{\sigma}{\mathrm{Y}}(q-p)\epsilon^2.$

" " AB $= -\frac{1}{4}\epsilon^2+\frac{p\epsilon^2}{3\mathrm{K}}-\frac{\sigma}{\mathrm{Y}}(q-p)\epsilon^2.$

" perpendicular to the plane $= \frac{p\epsilon^2}{3\mathrm{K}}+\frac{1}{\mathrm{Y}}(q-p)\epsilon^2.$

As in the experiments described above Y and σ were determined directly, it will be convenient to replace K from the equation $\frac{1}{3\mathrm{K}} = \frac{1-2\sigma}{\mathrm{Y}}$, and the secondary strains become

$$\left(\frac{1}{4}+\frac{1-\sigma}{\mathrm{Y}}p-\frac{\sigma}{\mathrm{Y}}q\right)\epsilon^2, \quad \left(-\frac{1}{4}+\frac{1-\sigma}{\mathrm{Y}}p-\frac{\sigma}{\mathrm{Y}}q\right)\epsilon^2, \quad \left(-\frac{2\sigma}{\mathrm{Y}}p+\frac{1}{\mathrm{Y}}q\right)\epsilon^2.$$

Equations Representing the Changes in the Dimensions of a Wire Subject to a Torque.

I am indebted to Sir Joseph Larmor for his kindness in indicating how the following equations should be formed and solved. Let us assume that we put on to a wire of length l and radius a a pure shear stress proportional to the distance r from the axis, and twisting length l through angle θ. Then in addition to the shear $\epsilon = r\theta/l$, this stress would produce in an element unconstrained by neighbouring material what we may term "free strains" with the values just found, which we may write as αr^2 radial; βr^2 transverse to the radius; and γr^2 longitudinal; where

$$\left.\begin{aligned}\alpha &= \left(-\frac{2\sigma}{Y}p+\frac{1}{Y}q\right)\frac{\theta^2}{l^2}\\ \beta &= \left(-\frac{1}{4}+\frac{1-\sigma}{Y}p-\frac{\sigma}{Y}q\right)\frac{\theta^2}{l^2}\\ \gamma &= \left(+\frac{1}{4}+\frac{1-\sigma}{Y}p-\frac{\sigma}{Y}q\right)\frac{\theta^2}{l^2}\end{aligned}\right\} \qquad (1)$$

If u is the actual radial displacement, and if w is the actual longitudinal displacement, the strains in addition to the shear ϵ are, in cylindrical co-ordinates,

$$du/dr, \qquad u/r, \quad \text{and} \quad dw/dz.$$

The differences between these actual strains and the "free strains," viz.,

$$e=\frac{du}{dr}-\alpha r^2, \qquad f=\frac{u}{r}-\beta r^2, \qquad g=\frac{dw}{dz}-\gamma r^2, \qquad (2)$$

imply "secondary stresses" in the wire due to adjustment of strain in neighbouring elements. Let these be denoted by R, Θ, W.

To find R, Θ, and W, we treat e, f, g, as if they were strains in an independent system. Putting $\Delta = e+f+g$, the equations are

$$R=\lambda\Delta+2\mu e, \qquad \Theta=\lambda\Delta+2\mu f, \qquad W=\lambda\Delta+2\mu g, \qquad (3)$$

where $\lambda = K-\frac{2}{3}n = \frac{\sigma Y}{(1+\sigma)(1-2\sigma)}$ and $\mu = n = \frac{Y}{2(1+\sigma)}$.

The forces R, Θ, and W must form a system in equilibrium, there being no external forces to balance. Considering the equilibrium of the element ABCD, fig. 5,

$$d(Rr\delta\theta)=\Theta\delta\theta\, dr, \quad \text{whence} \quad r\frac{dR}{dr}+R=\Theta. \qquad (4)$$

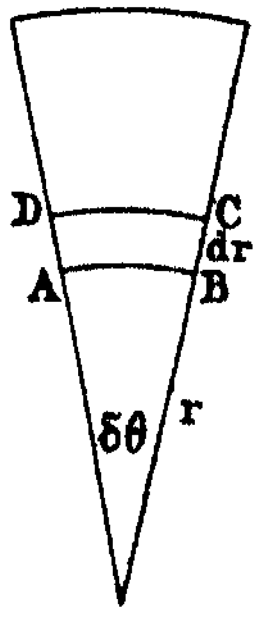

FIG. 5.

We obtain another equation by assuming that the wire is so gripped at each end that sections perpendicular to the axis remain perpendicular to the axis after twisting. Indeed, we have already assumed this in omitting equations for shear stress in (3). Hence w is independent of r and dw/dz is constant over a section for a given wire with a given twist. Let us put

$$dw/dz = h.$$

Further, the load is constant, so that

$$\int_0^a W r\, dr = 0. \qquad (5)$$

Substituting in (4) from (3) we obtain

$$r\frac{d^2u}{dr^2}+\frac{du}{dr}-\frac{u}{r}=\frac{2\lambda(\alpha+\beta+\gamma)+6\mu\alpha-2\mu\beta}{\lambda+2\mu}r^2. \tag{6}$$

By putting $u/r = v$, we easily find the solution

$$u = \mathrm{A}r^3+\mathrm{B}r+\mathrm{C}r^{-1}, \tag{7}$$

where
$$\mathrm{A}=\frac{2\lambda(\alpha+\beta+\gamma)+6\mu\alpha-2\mu\beta}{8(\lambda+2\mu)},$$

and B and C are arbitrary constants to be determined by the boundary conditions.

If the wire is unstrained in all parts before twisting, the solution applies with the same constants for all parts.

In order that $u = 0$ when $r = 0$, we must have $\mathrm{C} = 0$, so that

$$u = \mathrm{A}r^3+\mathrm{B}r. \tag{8}$$

When $r = a$, $\mathrm{R} = 0$.

Substituting from (8) in the value of R in (3), and putting $\mathrm{R} = 0$ when $r = a$, we get

$$2(\lambda+\mu)\mathrm{B}+\lambda h = \{\lambda(\alpha+\beta+\gamma)+2\mu\alpha-(4\lambda+6\mu)\mathrm{A}\}\,a^2. \tag{9}$$

From equation (5) we obtain another relation between B and h, when we substitute for u from (8) in W from (3) and integrate from $r = 0$ to $r = a$, viz.,

$$\lambda\mathrm{B}+(\tfrac{1}{2}\lambda+\mu)h = \{\tfrac{1}{4}\lambda(\alpha+\beta+\gamma)+\tfrac{1}{2}\mu\gamma-\lambda\mathrm{A}\}\,a^2, \tag{10}$$

and from (9) and (10) we can find B and h.

Since A is a linear function of α, β, and γ, and each of these is proportional to θ^2, h and B are proportional to θ^2. Substituting for B in (8), u is also proportional to θ^2. The theory, then, gives the parabolic law for the twisting of a wire initially unstrained both for lengthening and for side contraction. It also gives the lengthening and side contraction w/l and u/a for different wires of the same material as proportional to a^2.

So far the theory does not, of course, give any account of the fact that the wires examined are always unsymmetrical, that the effects always date from a point c, on the counter-clockwise side in the wires examined, c being different for w and u. This want of symmetry implies initial internal strain, probably, in reality, very complicated. Let us examine a simple case in which there is a core, radius a, twisted initially against a sheath, outer radius b, and let the opposing twists be respectively θ_c and θ_s. When we put a twist θ from outside on to the core as a whole the core is twisted through $\theta+\theta_c$, and the sheath through $\theta-\theta_s$. For the core and sheath respectively we have

$$u_c = \mathrm{A}r^3+\mathrm{B}r$$
$$u_s = \mathrm{A}'r^3+\mathrm{B}'r+\mathrm{C}'r^{-1},$$

where A is a linear function of α, β, γ, and therefore proportional to $(\theta+\theta_c)^2$ and A′ is the same function of α', β', γ', say, and therefore proportional to $(\theta-\theta_s)^2$.

To find the constants we have

$$\begin{aligned} u_c &= u_s \quad \text{when} \quad r = a, \\ \mathrm{R}_c &= \mathrm{R}_s \quad \text{,,} \quad \text{,,} \\ \mathrm{R}_s &= 0 \quad \text{,,} \quad r = b, \end{aligned}$$

and

$$\int_0^a \mathrm{W}_c r\,dr + \int_a^b \mathrm{W}_s r\,dr = 0.$$

These give us four equations to find B, B′, C′, h of the form (it appears needless to give the detailed work)—

$$\mathrm{B} = \mathrm{P}_1(\theta+\theta_c)^2+\mathrm{Q}_1(\theta-\theta_s)^2, \qquad \mathrm{C}' = \mathrm{P}_3(\theta+\theta_c)^2+\mathrm{Q}_3(\theta-\theta_s)^2,$$

$$\mathrm{B}' = \mathrm{P}_2(\theta+\theta_c)^2+\mathrm{Q}_2(\theta-\theta_s)^2, \qquad h = \mathrm{P}_4(\theta+\theta_c)^2+\mathrm{Q}_4(\theta-\theta_s)^2;$$

and, substituting for A′, B′, C′, in u_s, and putting $r = b$, we get

$$u_b = \mathrm{P}_5(\theta+\theta_c)^2+\mathrm{Q}_5(\theta-\theta_s)^2.$$

Both h and u_b are of the form

$$\mathrm{D}\theta^2+\mathrm{E}\theta+\mathrm{F},$$

where D does not contain θ_c or θ_s. As the parabolas depend only on D, E and F merely giving the position of the vertex, θ_c and θ_s only affect that position.

To find that position we may put $dh/d\theta = 0$ for the one, $du/d\theta = 0$ for the other, and since h and u are different functions of θ_c and θ_s the vertices will be at different points for the two quantities h and u.

Taking this simple case as a guide we shall assume that internal strain only affects the position and not the size of the parabola representing the change of linear dimensions on twisting.

Hence if we could obtain a wire without internal strain we should have

$$\mathrm{L}n^2 = w,$$

where L has the value found in the experiments on the actual, initially strained wire, and we may regard the values u/a and w/l for one turn as the values for a wire initially without internal strain.

The Values of p and q in the Secondary Stresses.

We are now able to find the values of p and q. For the known values of Y and σ enable us to find α, β and γ in equations (1) in terms of p and q

for a known twist, which we shall take as one turn, or as 2π in length $l = 160{\cdot}5$ cm. We also know λ and μ, since

$$\lambda = \sigma Y / (1+\sigma)(1-2\sigma) \quad \text{and} \quad \mu = n = Y/2(1+\sigma).$$

Substituting for λ, μ, α, β, and γ we can determine A in terms of p and q. Then from equations (9) and (10) we can find B and h in terms of p and q. Equating Aa^2+B to the observed value of u/a (which is negative), and h to the observed value of w/l, we have two linear equations in p and q.

The arithmetic is straightforward, though very lengthy, and may be omitted. I have used a slide rule in the calculations.

Using the values of the elastic constants Y and σ from Table II, and the values of u/a and w/l, on p. 548, I find for Wire I

$$p = 1{\cdot}67 \times 10^{12}, \qquad q = -0{\cdot}70 \times 10^{12},$$

so that the force perpendicular to the plane of the figure in fig. 4 is a tension and not a pressure.

The Pressure in the Direction of Propagation in Distortional Waves and the Longitudinal Waves Produced by the Pressure.

If we had a train of waves purely distortional, that is, a train in which the strain could be represented by a pure shear ϵ, there would be a pressure in the direction of propagation $(\frac{1}{2}n+p)\epsilon^2$. But as ϵ varies from point to point in the train, the pressure due to the shear strain varies, and there must be longitudinal disturbance, longitudinal waves, accompanying the distortional waves. The longitudinal strain implies that the material yields under the pressure, and the pressure will, in general, have a different value from that in a pure shear.

Let us represent the distortional train by

$$\epsilon = \eta \sin \frac{2\pi}{\lambda}(x-vt),$$

where $v^2 = n/\rho$ and η is the amplitude of the shear.

If ξ is the longitudinal displacement at the point where the shear is ϵ, $d\xi/dx$ is the elongation of the element about the point.

Now if we shear a cube, and remove the pressure $(\frac{1}{2}n+p)\epsilon^2$, the cube elongates in that direction, and if the dimensions in the two directions at right angles are maintained the same, the removal of the pressure produces elongation

$$\nu^{-1}(\tfrac{1}{2}n+p)\epsilon^2, \quad \text{where} \quad \nu = \lambda + 2\mu = K + \tfrac{4}{3}n.$$

This we may term the "free elongation" in the direction of propagation on the supposition that there is no change of length at right angles to it.

The pressure due to the shear falls from its full value $(\frac{1}{2}n+p)\epsilon^2$ to 0 while the elongation increases from 0 to its full value $\nu^{-1}(\frac{1}{2}n+p)\epsilon^2$. When the elongation is $d\xi/dx$ the pressure remaining is

$$\mathrm{P} = \frac{\nu^{-1}(\frac{1}{2}n+p)\epsilon^2 - d\xi/dx}{\nu^{-1}(\frac{1}{2}n+p)\epsilon^2}(\tfrac{1}{2}n+p)\epsilon^2 = (\tfrac{1}{2}n+p)\epsilon^2 - \nu\, d\xi/dx$$

$$= (\tfrac{1}{2}n+p)\eta^2 \sin^2\frac{2\pi}{\lambda}(x-vt) - \nu\, d\xi/dx.$$

The equation of motion for the longitudinal waves is

$$\rho\frac{d^2\xi}{dt^2} = -\frac{d\mathrm{P}}{dx} = -(\tfrac{1}{2}n+p)\eta^2\frac{2\pi}{\lambda}\sin\frac{4\pi}{\lambda}(x-vt) + \nu\, d^2\xi/dx^2,$$

an equation similar in form to that for the longitudinal waves which I have attempted to show must accompany light waves.*

If we put
$$\xi = \mathrm{A}\sin\frac{4\pi}{\lambda}(x-vt-\alpha),$$

and substitute in the above equation, we find on putting $x = 0$, $t = 0$, that $\alpha = 0$, and

$$\mathrm{A} = \frac{(\frac{1}{2}n+p)\eta^2\lambda}{8\pi(\rho v^2-\nu)},$$

or if v' is the velocity of free longitudinal waves, since $\rho v'^2 = \nu$ and $v'^2 > v^2$,

$$\mathrm{A} = -\frac{(\frac{1}{2}n+p)\eta^2\lambda}{8\pi\rho(v'^2-v^2)}.$$

If we substitute for $d\xi/dx$ in P, we get

$$\mathrm{P} = \tfrac{1}{2}(\tfrac{1}{2}n+p)\eta^2\left\{1-\cos\frac{4\pi}{\lambda}(x-vt)\right\} - \nu\mathrm{A}\frac{4\pi}{\lambda}\cos\frac{4\pi}{\lambda}(x-vt).$$

We may regard this as made up by a steady pressure $\frac{1}{2}(\frac{1}{2}n+p)\eta^2$ and a purely periodic pressure, of which the average is zero.

If E is the energy per cubic centimetre at any point in the distortional waves, it is half kinetic energy, half strain energy. The latter is $\frac{1}{2}n\epsilon^2$, so that the total is $n\epsilon^2$ or

$$\mathrm{E} = n\eta^2\sin^2\frac{2\pi}{\lambda}(x-vt) = \tfrac{1}{2}n\eta^2\left\{1-\cos\frac{4\pi}{\lambda}(x-vt)\right\}.$$

Then the average value is

$$\bar{\mathrm{E}} = \tfrac{1}{2}n\eta^2.$$

If we denote the average pressure by $\bar{\mathrm{P}}$,

$$\bar{\mathrm{P}} = \frac{\frac{1}{2}n+p}{n}\bar{\mathrm{E}}.$$

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* 'Roy. Soc. Proc.,' A, vol. 85, p. 474.

If we use the values of n and p found for Wire I, we find

$$\bar{P} = 2{\cdot}50\,\bar{E}.$$

If we put the energy per cubic centimetre in the longitudinal waves as $\frac{\rho}{2}\left(\frac{d\xi}{dt}\right)^2 + \frac{\nu}{2}\left(\frac{d\xi}{dx}\right)^2$, we find that

$$\frac{\text{Average energy in longitudinal waves}}{\text{Average energy in distortional waves}} = \frac{1}{8\rho}\,\frac{v'^2+v^2}{(v'^2-v^2)^2}\,\frac{(\frac{1}{2}n+p)^2}{n}\,\eta^2,$$

so that the ratio is proportional to η^2 and therefore in any actual waves it is very small.

The pressures at right angles to the line of propagation will not produce any disturbance in a wave front where η is constant. Round the edges of the wave front, however, where η is diminishing as we go outwards, they may have effects, and it appears likely that they may give rise to disturbances propagated sideways.

I have much pleasure in recording my hearty thanks to Mr. G. O. Harrison, mechanic in the laboratory workshop, for his great help in planning the apparatus used in the experiments described in this paper, for his skill in constructing it, and for his assistance in making the observations.

On the Self-Induction of Electric Currents in a Thin Anchor-Ring.

By Lord RAYLEIGH, O.M., F.R.S.

(Received March 5,—Read March 21, 1912.)

In their useful compendium of "Formulæ and Tables for the Calculation of Mutual and Self-Inductance,"* Rosa and Cohen remark upon a small discrepancy in the formulæ given by myself† and by M. Wien‡ for the self-induction of a coil of circular cross-section over which the current is *uniformly distributed.* With omission of n, representative of the number of windings, my formula was

$$L = 4\pi a\left[\log\frac{8a}{\rho}-\frac{7}{4}+\frac{\rho^2}{8a^2}\left(\log\frac{8a}{\rho}+\frac{1}{3}\right)\right], \tag{1}$$

where ρ is the radius of the section and a that of the circular axis. The first two terms were given long before by Kirchhoff.§ In place of the fourth term within the bracket, viz., $+\frac{1}{24}\rho^2/a^2$, Wien found $-\cdot 0083\rho^2/a^2$. In either case a correction would be necessary in practice to take account of the space occupied by the insulation. Without, so far as I see, giving a reason, Rosa and Cohen express a preference for Wien's number. The difference is of no great importance, but I have thought it worth while to repeat the calculation and I obtain the same result as in 1881. A confirmation after 30 years, and without reference to notes, is perhaps almost as good as if it were independent. I propose to exhibit the main steps of the calculation and to make extension to some related problems.

The starting point is the expression given by Maxwell‖ for the mutual induction M between two neighbouring co-axial circuits. For the present purpose this requires transformation, so as to express the inductance in terms of the situation of the elementary circuits relatively to the circular axis. In the figure, O is the centre of the circular axis, A the centre of a section B through the axis of symmetry, and the position of any point P of the section is given by polar co-ordinates relatively to A, viz., by PA (ρ)

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* 'Bulletin of the Bureau of Standards, Washington,' 1908, vol. 3, No. 1.

† 'Roy. Soc. Proc.,' 1881, vol. 32, p. 104; 'Scientific Papers,' vol. 2, p. 15.

‡ 'Ann. d. Physik,' 1894, vol. 53, p. 934; it would appear that Wien did not know of my earlier calculation.

§ 'Pogg. Ann.,' 1864, vol. 121, p. 551.

‖ 'Electricity and Magnetism,' § 705.

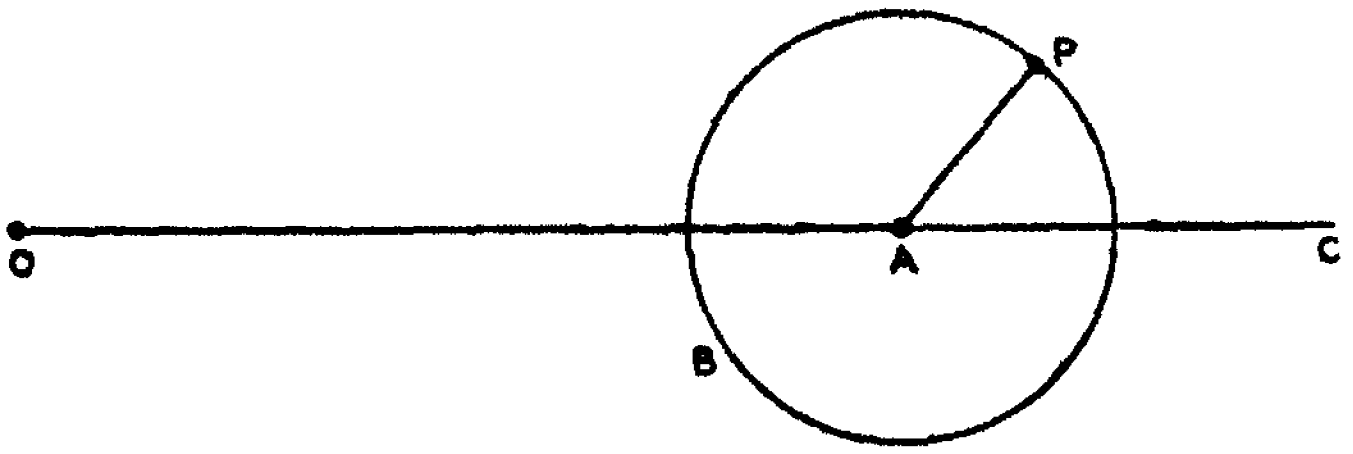
and by the angle PAC (ϕ). If ρ_1, ϕ_1; ρ_2, ϕ_2, be the co-ordinates of two points of the section P_1, P_2, the mutual induction between the two circular circuits represented by P_1, P_2 is approximately

$$\begin{aligned}\frac{M_{12}}{4\pi a} = &\left\{1 + \frac{\rho_1\cos\phi_1 + \rho_2\cos\phi_2}{2a} + \frac{\rho_1^2 + \rho_2^2 + 2\rho_1^2\sin^2\phi_1 + 2\rho_2^2\sin^2\phi_2}{16a^2}\right.\\ &\left.-\frac{2\rho_1\rho_2\cos(\phi_1-\phi_2) + 4\rho_1\rho_2\sin\phi_1\sin\phi_2}{16a^2}\right\}\log\frac{8a}{r}\\ &-2-\frac{\rho_1\cos\phi_1+\rho_2\cos\phi_2}{2a}\\ &+\frac{3(\rho_1^2+\rho_2^2)-4(\rho_1^2\sin^2\phi_1+\rho_2^2\sin^2\phi_2)+2\rho_1\rho_2\cos(\phi_1-\phi_2)}{16a^2}, \quad (2)\end{aligned}$$

in which r, the distance between P_1 and P_2, is given by

$$r^2 = \rho_1^2 + \rho_2^2 - 2\rho_1\rho_2\cos(\phi_1 - \phi_2). \quad (3)$$

Further details will be found in Wien's memoir; I do not repeat them because I am in complete agreement so far.



For the problem of a current uniformly distributed we are to integrate (2) twice over the area of the section. Taking first the integrations with respect to ϕ_1, ϕ_2, let us express

$$\frac{1}{4\pi^2}\int_{-\pi}^{+\pi}\int_{-\pi}^{+\pi}\frac{M_{12}}{4\pi a}\,d\phi_1 d\phi_2, \quad (4)$$

of which we can also make another application. The integration of the terms which do not involve $\log r$ is elementary. For those which do involve $\log r$ we may conveniently replace ϕ_2 by $\phi_1 + \phi$, where $\phi = \phi_2 - \phi_1$, and take first the integration with respect to ϕ, ϕ_1 being constant. Subsequently we integrate with respect to ϕ_1.

It is evident that the terms in (2) which involve the first power of ρ vanish in the integration. For a change of ϕ_1, ϕ_2, into $\pi - \phi_1$, $\pi - \phi_2$, respectively reverses $\cos\phi_1$ and $\cos\phi_2$, while it leaves r unaltered. The definite integrals required for the other terms are*

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* Todhunter's 'Int. Calc.,' §§ 287, 289.

$$\int_{-\pi}^{+\pi}\log(\rho_1^2+\rho_2^2-2\rho_1\rho_2\cos\phi)\,d\phi = \text{greater of } 4\pi\log\rho_2 \text{ and } 4\pi\log\rho_1, \tag{5}$$

$$\int_{-\pi}^{+\pi}\cos m\phi\log(\rho_1^2+\rho_2^2-2\rho_1\rho_2\cos\phi)\,d\phi$$
$$= -\frac{2\pi}{m}\times\text{smaller of }\left(\frac{\rho_2}{\rho_1}\right)^m\text{ and }\left(\frac{\rho_1}{\rho_2}\right)^m, \tag{6}$$

m being an integer. Thus

$$\frac{1}{4\pi^2}\iint\log r\,d\phi_1 d\phi_2 = \frac{1}{4\pi^2}\int_{-\pi}^{+\pi}d\phi_1\int_{-\pi}^{+\pi}d\phi\log r = \text{greater of }\log\rho_2\text{ and }\log\rho_1. \tag{7}$$

So far as the more important terms in (4)—those which do not involve ρ as a factor—we have at once

$$\log(8a)-2-\text{greater of }\log\rho_2\text{ and }\log\rho_1. \tag{8}$$

If ρ_2 and ρ_1 are equal, this becomes

$$\log(8a/\rho)-2. \tag{9}$$

We have now to consider the terms of the second order in (2). The contribution which these make to (4) may be divided into two parts. The first, not arising from the terms in $\log r$, is easily found to be

$$\frac{\rho_1^2+\rho_2^2}{8a^2}[\log(8a)+\tfrac{1}{2}]. \tag{10}$$

The difference between Wien's number and mine arises from the integration of the terms in $\log r$, so that it is advisable to set out these somewhat in detail. Taking the terms in order, we have as in (7)

$$\frac{1}{4\pi^2}\int_{-\pi}^{+\pi}\int_{-\pi}^{+\pi}\log r\,d\phi_1 d\phi_2 = \text{greater of }\log\rho_2\text{ and }\log\rho_1. \tag{11}$$

In like manner

$$\frac{1}{4\pi^2}\iint\sin^2\phi_1\log r\,d\phi_1 d\phi_2 = \tfrac{1}{2}\,[\text{greater of }\log\rho_2\text{ and }\log\rho_1], \tag{12}$$

and $\frac{1}{4\pi^2}\iint\sin^2\phi_2\log r\,d\phi_1 d\phi_2$ has the same value. Also by (6), with $m=1$,

$$\frac{1}{4\pi^2}\iint\cos(\phi_2-\phi_1)\log r\,d\phi_1 d\phi_2 = -\tfrac{1}{2}\,[\text{smaller of }\rho_2/\rho_1\text{ and }\rho_1/\rho_2]. \tag{13}$$

Finally
$$\frac{1}{4\pi^2}\iint\sin\phi_1\sin\phi_2\log r\,d\phi_1 d\phi_2$$
$$= \frac{1}{4\pi^2}\int_{-\pi}^{+\pi}d\phi_1\sin\phi_1\int_{-\pi}^{+\pi}(\sin\phi_1\cos\phi+\cos\phi_1\sin\phi)\log r\,d\phi$$
$$= -\tfrac{1}{4}\,[\text{smaller of }\rho_2/\rho_1\text{ and }\rho_1/\rho_2]. \tag{14}$$

Thus altogether the terms in (2) of the second order involving $\log r$ yield in (4)

$$-\frac{\rho_1^2+\rho_2^2}{8a^2}[\text{greater of } \log\rho_2 \text{ and } \log\rho_1]-\frac{\rho_1\rho_2}{8a^2}\left[\text{smaller of } \frac{\rho_2}{\rho_1} \text{ and } \frac{\rho_2}{\rho_1}\right]. \quad (15)$$

The complete value of (4) to this order of approximation is found by addition of (8), (10), and (15).

By making ρ_2 and ρ_1 equal we obtain at once for the self-induction of a current limited to the circumference of an anchor-ring, and uniformly distributed over that circumference,

$$\mathrm{L} = 4\pi a\left[\left(1+\frac{\rho^2}{4a^2}\right)\log\frac{8a}{\rho}-2\right], \quad (16)$$

ρ being the radius of the circular section. The value of L for this case, when ρ^2 is neglected, was virtually given by Maxwell.*

When the current is uniformly distributed over the area of the section we have to integrate again with respect to ρ_1 and ρ_2 between the limits 0 and ρ in each case. For the more important terms we have from (8)

$$\begin{aligned}\frac{1}{\rho^4}\iint & d\rho_1^2 d\rho_2^2\,[\log 8a-2-\text{greater of } \log\rho_2 \text{ and } \log\rho_1] \\ &= \log 8a-2-\frac{1}{2\rho^4}\int d\rho_1^2\,[\log\rho_1^2\,.\,\rho_1^2+\rho^2(\log\rho^2-1)-\rho_1^2(\log\rho_1^2-1)] \\ &= \log 8a-2-\log\rho+\frac{1}{4} = \log\frac{8a}{\rho}-\frac{7}{4}. \quad (17)\end{aligned}$$

A similar operation performed upon (10) gives

$$\frac{\log(8a)+\frac{1}{2}}{8a^2\rho^4}\iint(\rho_1^2+\rho_2^2)\,d\rho_1^2 d\rho_2^2 = \frac{\log(8a)+\frac{1}{2}}{8}\frac{\rho^2}{a^2}. \quad (18)$$

In like manner, the first part of (15) yields

$$-\frac{\rho^2}{16a^2}(\log\rho^2-\tfrac{1}{3}).$$

For the second part we have

$$-\frac{1}{8a^2\rho^4}\iint d\rho_1^2 d\rho_2^2\,[\text{smaller of } \rho_2^2, \rho_1^2] = -\frac{\rho^2}{24a^2};$$

thus altogether from (15)

$$-\frac{\rho^2}{8a^2}(\log\rho+\tfrac{1}{6}). \quad (19)$$

The terms of the second order are accordingly, by addition of (18) and (19),

$$\frac{\rho^2}{8a^2}\left(\log\frac{8a}{\rho}+\tfrac{1}{3}\right). \quad (20)$$

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* 'Electricity and Magnetism,' §§ 692, 706.

To this are to be added the leading terms (17); whence, introducing $4\pi a$, we get finally the expression for L already stated in (1).

It must be clearly understood that the above result, and the corresponding one for a *hollow* anchor-ring, depend upon the assumption of a uniform distribution of current, such as is approximated to when the coil consists of a great number of windings of wire insulated from one another. If the conductor be solid and the currents due to induction, the distribution will, in general, not be uniform. Under this head Wien considers the case where the currents are due to the variation of a homogeneous magnetic field, parallel to the axis of symmetry, and where the distribution of currents is governed by *resistance*, as will happen in practice when the variations are slow enough. In an elementary circuit the electromotive force varies as the square of the radius and the resistance as the first power. Assuming as before that the whole current is unity, we have merely to introduce into (4) the factors

$$\frac{(a+\rho_1\cos\phi_1)(a+\rho_2\cos\phi_2)}{a^2}, \tag{21}$$

M_{12} retaining the value given in (2).

The leading term in (21) is unity, and this, when carried into (14), will reproduce the former result. The term of the first order in ρ in (21) is $(\rho_1\cos\phi_1+\rho_2\cos\phi_2)/a$, and this must be combined with the terms of order ρ^0 and ρ^1 in (2). The former, however, contributes nothing to the integral. The latter yield in (4)

$$\frac{\rho_1^2+\rho_2^2}{4a^2}\{\log 8a-1-\text{greater of }\log\rho_1\text{ and }\log\rho_2\}+\frac{\text{smaller of }\rho_1^2\text{ and }\rho_2^2}{4a^2}. \tag{22}$$

The term of the second order in (21), viz., $\rho_1\rho_2/a^2 \,.\, \cos\phi_1\cos\phi_2$, needs to be combined only with the leading term in (2). It yields in (4)

$$\frac{\text{smaller of }\rho_1^2\text{ and }\rho_2^2}{4a^2}. \tag{23}$$

If ρ_1 and ρ_2 are equal (ρ), the additional terms expressed by (22), (23), become

$$\frac{\rho^2}{2a^2}\log\frac{8a}{\rho}. \tag{24}$$

If (24), multiplied by $4\pi a$, be added to (16), we shall obtain the self-induction for a shell (of uniform infinitesimal thickness) in the form of an anchor-ring, the currents being excited in the manner supposed. The result is

$$L = 4\pi a\left\{\left(1+\frac{3\rho^2}{4a^2}\right)\log\frac{8a}{\rho}-2\right\}. \tag{25}$$

We now proceed to consider the solid ring. By (22), (23) the terms, additional to those previously obtained on the supposition that the current was uniformly distributed, are

$$\frac{1}{\rho^4}\iint d\rho_1^2 d\rho_2^2\left[\frac{\text{smaller of } \rho_1^2 \text{ and } \rho_2^2}{2a^2}\right.$$
$$\left.+\frac{\rho_1^2+\rho_2^2}{4a^2}\{\log 8a-1-\text{greater of } \log\rho_1 \text{ and } \log\rho_2\}\right]. \qquad (26)$$

The first part of this is $\rho^2/6a^2$, and the second is $\frac{\rho^2}{4a^2}\{\log 8a-1-\log\rho+\frac{1}{6}\}$. The additional terms are accordingly

$$\frac{\rho^2}{4a^2}\left\{\log\frac{8a}{\rho}-\frac{1}{6}\right\}. \qquad (27)$$

These multiplied by $4\pi a$ are to be added to (1). We thus obtain

$$L = 4\pi a\left[\log\frac{8a}{\rho}-\frac{7}{4}+\frac{3\rho^2}{8a^2}\log\frac{8a}{\rho}\right] \qquad (28)$$

for the self-induction of the solid ring when currents are slowly generated in it by uniform magnetic forces parallel to the axis of symmetry. In Wien's result for this case there appears an additional term within the bracket equal to $-0{\cdot}092\,\rho^2/a^2$.

A more interesting problem is that which arises when the alternations in the magnetic field are rapid instead of slow. Ultimately the distribution of current becomes independent of *resistance*, and is determined by induction alone. A leading feature is that the currents are *superficial*, although the ring itself may be solid. They remain, of course, symmetrical with respect to the straight axis, and to the plane which contains the circular axis.

The magnetic field may be supposed to be due to a current x_1 in a circuit at a distance, and the whole energy of the field may be represented by

$$T = \tfrac{1}{2}M_{11}x_1^2+\tfrac{1}{2}M_{22}x_2^2+\tfrac{1}{2}M_{33}x_3^2+\ldots+M_{12}x_1x_2+M_{13}x_1x_3+\ldots+M_{23}x_2x_3$$
$$+\ldots, \qquad (29)$$

x_2, x_3, etc., being currents in other circuits where no independent electromotive force acts. If x_1 be regarded as given, the corresponding values of x_2, x_3, ..., are to be found by making T a minimum. Thus

$$\left.\begin{aligned} M_{12}x_1+M_{22}x_2+M_{32}x_3+\ldots &= 0,\\ M_{13}x_1+M_{23}x_2+M_{33}x_3+\ldots &= 0,\end{aligned}\right\} \qquad (30)$$

and so on, are the equations by which x_2, etc., are to be found in terms of x_1. What we require is the corresponding value of T′, formed from T by omission of the terms containing x_1.

The method here sketched is general. It is not necessary that x_2, etc., be currents in particular circuits. They may be regarded as generalised co-ordinates, or rather velocities, by which the kinetic energy of the system is defined.

For the present application we suppose that the distribution of current round the circumference of the section is represented by

$$\{\alpha_0+\alpha_1\cos\phi_1+\alpha_2\cos 2\phi_1+\ldots\}\frac{d\phi_1}{2\pi}, \tag{31}$$

so that the total current is α_0. The doubled energy, so far as it depends upon the interaction of the ring currents, is

$$\frac{1}{4\pi^2}\iint(\alpha_0+\alpha_1\cos\phi_1+\alpha_2\cos 2\phi_1+\ldots)\,(\alpha_0+\alpha_1\cos\phi_2+\ldots)\,\mathrm{M}_{12}\,d\phi_1\,d\phi_2, \tag{32}$$

where M_{12} has the value given in (2), simplified by making ρ_1 and ρ_2 both equal to ρ. To this has to be added the double energy arising from the interaction of the ring currents with the primary current. For each element of the ring currents (31) we have to introduce a factor proportional to the area of the circuit, viz., $\pi(a+\rho\cos\phi_1)^2$. This part of the double energy may thus be taken to be

$$\mathrm{H}\int d\phi_1\,(a+\rho\cos\phi_1)^2(\alpha_0+\alpha_1\cos\phi_1+\alpha_2\cos 2\phi_1+\ldots),$$

that is

$$2\pi\mathrm{H}\,\{(a^2+\tfrac{1}{2}\rho^2)\,\alpha_0+a\rho\alpha_1+\tfrac{1}{4}\rho^2\alpha_2\}, \tag{33}$$

α_3, etc., not appearing. The sum of (33) and (32) is to be made a minimum by variation of the α's.

We have now to evaluate (32). The coefficient of α_0^2 is the quantity already expressed in (16). For the other terms it is not necessary to go further than the first power of ρ in (2). We get

$$4\pi a\left[\alpha_0^2\left\{\log\frac{8a}{\rho}\left(1+\frac{\rho^2}{4a^2}\right)-2\right\}+\tfrac{1}{4}(\alpha_1^2+\tfrac{1}{2}\alpha_2^2+\tfrac{1}{3}\alpha_3^2+\ldots)\right.$$
$$\left.+\frac{\rho}{a}\left\{\frac{\alpha_0\alpha_1}{2}\left(\log\frac{8a}{\rho}-1\right)+\frac{\alpha_1}{8}(2\alpha_0+\alpha_2)+\frac{\alpha_2}{2\,.\,8}(\alpha_1+\alpha_3)+\frac{\alpha_3}{3\,.\,8}(\alpha_2+\alpha_4)+\ldots\right\}\right], \tag{34}$$

Differentiating the sum of (33), (34), with respect to α_0, α_1, etc., in turn, we find

$$\mathrm{H}\,(a^2+\tfrac{1}{2}\rho^2)+4a\alpha_0\left\{\log\frac{8a}{\rho}\left(1+\frac{\rho^2}{4a^2}\right)-2\right\}+\rho\alpha_1\left(\log\frac{8a}{\rho}-\frac{1}{2}\right)=0, \tag{35}$$

$$\mathrm{H}\rho+\alpha_1+\frac{\rho}{a}\left\{\alpha_0\left(\log\frac{8a}{\rho}-\frac{1}{2}\right)+\frac{3\alpha_2}{8}\right\}=0, \tag{36}$$

$$\mathrm{H}\rho^2+2a\alpha_2+\rho\left(\frac{3\alpha_1}{2}+\frac{5\alpha_3}{6}\right)=0. \tag{37}$$

The leading term is, of course, α_0. Relatively to this, α_1 is of order ρ, α_2 of order ρ^2, and so on. Accordingly, α_2, α_3, etc., may be omitted entirely from (34), which is only expected to be accurate up to ρ^2 inclusive. Also, in α_1 only the leading term need be retained.

The ratio of α_1 to α_0 is to be found by elimination of H between (35), (36). We get

$$\frac{\alpha_1}{\alpha_0} = \frac{\rho}{a}\left\{3\log\frac{8a}{\rho} - \frac{15}{2}\right\}. \tag{38}$$

Substituting this in (34), we find as the coefficient of self-induction

$$L = 4\pi a\left[\log\frac{8a}{\rho}\left(1+\frac{\rho^2}{4a^2}\right) - 2 + \frac{\rho^2}{4a^2}\left(3\log\frac{8a}{\rho} - \frac{15}{2}\right)\left(5\log\frac{8a}{\rho} - \frac{17}{2}\right)\right]. \tag{39}$$

The approximate value of α_0 in terms of H is

$$\alpha_0 = -\frac{Ha}{4\left(\log\frac{8a}{\rho} - 2\right)}. \tag{40}$$

A closer approximation can be found by elimination of α_1 between (35), (36).

In (39) the currents are supposed to be induced by the variation (in time) of an unlimited uniform magnetic field. A problem, simpler from the theoretical point of view, arises if we suppose the uniform field to be limited to a cylindrical space co-axial with the ring, and of diameter less than the smallest diameter of the ring $(2a-2\rho)$. Such a field may be supposed to be due to a cylindrical current sheet, the length of the cylinder being infinite. The ring currents to be investigated are those arising from the instantaneous abolition of the current sheet and its conductor.

If πb^2 be the area of the cylinder, (33) is replaced simply by

$$H\int d\phi_1\, b^2(\alpha_0 + \alpha_1\cos\phi_1 + \ldots) = 2\pi H b^2\alpha_0. \tag{41}$$

The expression (34) remains unaltered and the equations replacing (35), (36), are thus

$$Hb^2 + 4a\alpha_0\left\{\log\frac{8a}{\rho}\left(1+\frac{\rho^2}{4a^2}\right) - 2\right\} + \rho\alpha_1\left(\log\frac{8a}{\rho} - \frac{1}{2}\right) = 0. \tag{42}$$

$$\alpha_1 + \frac{\rho}{a}\left(\log\frac{8a}{\rho} - \frac{1}{2}\right)\alpha_0 = 0. \tag{43}$$

The introduction of (43) into (34) gives for the coefficient of self-induction in this case—

$$L = 4\pi a\left[\log\frac{8a}{\rho}\left(1+\frac{\rho^2}{4a^2}\right) - 2 - \frac{\rho^2}{4a^2}\left(\log\frac{8a}{\rho} - \frac{1}{2}\right)^2\right]. \tag{44}$$

It will be observed that the sign of α_1/α_0 is different in (38) and (43).

The peculiarity of the problem last considered is that the primary current occasions no magnetic force at the surface of the ring. The consequences were set out 40 years ago by Maxwell in a passage* whose significance was very slowly appreciated. "In the case of a current sheet of no resistance, the surface integral of magnetic induction remains constant at every point of the current sheet.

"If, therefore, by the motion of magnets or variations of currents in the neighbourhood, the magnetic field is in any way altered, electric currents will be set up in the current sheet, such that their magnetic effect, combined with that of the magnets or currents in the field, will maintain the normal component of magnetic induction at every point of the sheet unchanged. If at first there is no magnetic action, and no currents in the sheet, then the normal component of magnetic induction will always be zero at every point of the sheet.

"The sheet may therefore be regarded as impervious to magnetic induction, and the lines of magnetic induction will be deflected by the sheet exactly in the same way as the lines of flow of an electric current in an infinite and uniform conducting mass would be deflected by the introduction of a sheet of the same form made of a substance of infinite resistance.

"If the sheet forms a closed or an infinite surface, no magnetic actions which may take place on one side of the sheet will produce any magnetic effect on the other side."

All that Maxwell says of a current sheet is, of course, applicable to the surface of a perfectly conducting solid, such as our anchor-ring may be supposed to be. The currents left in the ring after the abolition of the primary current must be such that the magnetic force due to them is *wholly tangential* to the surface of the ring. Under this condition $\int_{-\pi}^{+\pi} \mathrm{M}_{12}\, d\phi_2$ must be independent of ϕ_1, and we might have investigated the problem upon this basis.

In Maxwell's notation α, β, γ, denote the components of magnetic force, and the whole energy of the field T is given by

$$\mathrm{T} = \frac{1}{8\pi}\iiint(\alpha^2+\beta^2+\gamma^2)\, dx\, dy\, dz = \tfrac{1}{2}\mathrm{L}\alpha_0^2. \qquad (45)$$

Moreover α_0, the total current, multiplied by 4π is equal to the "circulation" of magnetic force round the ring. In this form our result admits of immediate application to the hydrodynamical problem of the circulation of incompressible frictionless fluid round a solid having the form of the ring; for the components of velocity u, v, w, are subject to precisely the same conditions as are α, β, γ. If the density be unity, the kinetic energy T of the motion has the expression

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* 'Electricity and Magnetism,' §§ 654, 655. Compare my "Acoustical Observations," 'Phil. Mag.,' 1882, vol. 13, p. 340; 'Scientific Papers,' vol. 2, p. 99.

$$T = \frac{L}{8\pi} \times (\text{circulation})^2, \tag{46}$$

L having the value given in (44).

P.S., March 4.—Sir W. D. Niven, who in 1881 verified some other results for self-induction—those numbered (11), (12) in the paper referred to—has been good enough to confirm the formulæ (1), (28) of the present communication, in which I differ from M. Wien.

The Diffusion and Mobility of Ions in a Magnetic Field.

By John S. Townsend, F.R.S., Wykeham Professor of Physics, Oxford.

(Received March 11,—Read April 25, 1912.)

1. When the motion of ions in a gas takes place in a magnetic field the rates of diffusion and the velocities due to an electric force may be determined by methods similar to those given in a previous paper.*

The effect of the magnetic field may be determined by considering the motion of each ion between collisions with molecules. The magnetic force causes the ions to be deflected in their free paths, and when no electric force is acting the paths are spirals, the axes being along the direction of the magnetic force. If H be the intensity of the magnetic field, e the charge, and m the mass of an ion, then the radius r of the spiral is mv/He, v being the velocity in the direction perpendicular to H. The distance that the ion travels in the interval between two collisions in a direction normal to the magnetic force is a chord of the circle of radius r. The average lengths of these chords may be reduced to any fraction of the projection of the mean free path in the direction of the magnetic force, so that the rate of diffusion of ions in the directions perpendicular to the magnetic force is less than the rate of diffusion in the direction of the force.

In the previous paper it has been shown that the coefficient of diffusion K is a measure of the rate of increase of the mean square R^2 of the distance of any distribution from any point, dR^2/dt being equal to 6K. Since

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* 'Roy. Soc. Proc.,' February, 1912, vol. 86.

$R^2 = x^2+y^2+z^2$ it follows that $2K = dx^2/dt$, and $4K = d\rho^2/dt$, where ρ^2 is the mean of the squares of the distances of the ions from the axis of z.

When a magnetic force H is applied in the direction of the axis of z, the rate of diffusion K_h in the directions perpendicular to z is less than the rate of diffusion K along z, which is unaltered by the magnetic field. As the phenomena are of special interest in connection with negative ions in the electronic state when magnetic fields produce large effects, the collisions with molecules may be supposed to affect the motion of the ions in the same way as the motion of small bodies is affected by colliding with comparatively large particles. All directions of motion of an ion after collision with molecules may therefore be supposed to be equally probable, so that the mean values of the velocities of the ions after colliding will be zero. Since the magnetic field only alters the direction of motion, the number of collisions that an ion makes per second is not affected, and the intervals between the collisions will be distributed as in the ordinary case, and will have the same mean value T. The number of intervals that exceed the time t out of a total number N will be $Ne^{-t/T}$.

In the following investigations two expressions occur which may be found in terms of the mean time between collisions. These are the series of cosines: $\cos\omega t_1 + \cos\omega t_2 + \text{etc.}$; and the series of sines: $\sin\omega t_1 + \sin\omega t_2 + \text{etc.}$, t_1, t_2, etc., being intervals between a large number N of consecutive collisions that an ion makes with molecules. The number of intervals that lie between the values t and $t+dt$ is $\frac{N}{T}e^{-t/T}dt$, so that the series of cosines may be expressed as the integral

$$\frac{N}{T}\int_0^\infty \cos\omega t\, e^{-t/T}dt,$$

This expression may be integrated by parts and its value is $N/(1+\omega^2T^2)$. Similarly, the series of sines will be found to be equal to $N\omega T/(1+\omega^2T^2)$.

2. The rate of increase of the mean square of the distance of any distribution from the axis of z, $d\rho^2/dt$, may be determined by considering the motion of an ion parallel to the plane of xy.

Let x and y be the ordinates of an ion at any time t after a collision. The equations of motion are—

$$m\frac{d^2x}{dt^2} = -He\frac{dy}{dt}, \qquad m\frac{d^2y}{dt^2} = He\frac{dx}{dt},$$

and the velocities $\dot{x}$ and $\dot{y}$ are given by equations of the form

$$m^2\frac{d^2\dot{x}}{dt^2} + H^2e^2\dot{x} = 0,$$

so that $\dot{x} = A\sin(\omega t+\alpha)$ and $\dot{y} = -A\cos(\omega t+\alpha)$.

Let $\dot{x}_1, \dot{y}_1$ be the velocities at the beginning of the first interval, and let the first collision occur in a time t_1; $\dot{x}_2, \dot{y}_2$ the velocities after the first collision, and t_2 the interval between the first and second collision, etc.

In the first interval, the distances δx_1 and δy_1 traversed by the ions are

$$\delta x_1 = \frac{A}{\omega}[\cos\alpha_1 - \cos(\omega t_1+\alpha_1)] \quad \text{and} \quad \delta y_1 = \frac{A}{\omega}[\sin\alpha_1 - \sin(\omega t_1+\alpha_1)].$$

Let x_0, y_0 be the initial position of the ion, then after the time $NT = t_1+t_2$ + etc., the position will be

$$x_0 + \sum_{s=1}^{s=N}\delta x_s \quad \text{and} \quad y_0 + \sum_{s=1}^{s=N}\delta y_s,$$

and the square of the distance from the axis will have increased by the amount

$$2x_0\Sigma\,\delta x_s + 2y_0\Sigma\,\delta y_s + \Sigma(\delta x_s)^2 + \Sigma\,(\delta y_s)^2 + 2\Sigma\,(\delta x_r\delta x_s + \delta y_r\delta y_s).$$

The latter terms are zero, since, on the average, the sum of the cosines of the angles which any path makes with the consecutive paths vanishes.

Hence, for any ion, the square of the distance changes by the amount

$$2x_0\Sigma\,\delta x_s + 2y_0\Sigma\,\delta y_s + \Sigma(\delta x_s)^2 + \Sigma(\delta y_s)^2.$$

For a large number of ions starting from the point x_0, y_0, the average values of $\Sigma\,\delta x_s$ and $\Sigma\,\delta y_s$ vanish, since the ions are free to move in all directions. Hence the rate of change in the mean square of the distance of the distribution from the axis $d\rho^2/dt$ is $[\Sigma(\delta x_s)^2 + \Sigma(\delta y_s)^2]/NT$.

Substituting for δx_s and δy_s their values, the quantity $d\rho^2/dt$ becomes $\frac{2}{NT\omega^2}\Sigma\,A_s^2(1-\cos\omega t_s)$.

The velocities A_s are independent of the times t_s, so that the mean value of A^2 may be substituted for A_s^2 in this expression. Also, since A_s is the velocity in the plane xy, the mean value of A_s^2 is $\frac{2}{3}V^2$, V being the mean velocity of agitation of the ions; and, since the series of cosines $\Sigma\cos\omega t_s$, is equal to $N/(1+\omega^2T^2)$, the above expression reduces to

$$\frac{d\rho^2}{dt} = \frac{2N}{NT\omega^2} \times \frac{2V^2}{3} \times \frac{\omega^2T^2}{1+\omega^2T^2} = \frac{4V^2T}{3(1+\omega^2T^2)}.$$

The rate of diffusion K along the direction of the magnetic force is $\frac{1}{3}\lambda V$ or $\frac{1}{3}V^2T$. Hence

$$\frac{d\rho^2}{dt} = \frac{4K}{1+\omega^2T^2},$$

3. The motion of the ions may therefore be expressed in the usual form by the equations

$$\frac{nu}{K_h} = -\frac{dn}{dx}, \quad \frac{nv}{K_h} = -\frac{dn}{dy}, \quad \frac{nw}{K} = -\frac{dn}{dz}.$$

The change of the number of ions n per cubic centimetre at any point is

$$-\frac{dn}{dt} = \frac{d(nu)}{dx}+\frac{d(nv)}{dy}+\frac{d(nw)}{dz} = \mathrm{K}_h\left(\frac{d^2n}{dx^2}+\frac{d^2n}{dy^2}\right)+\mathrm{K}\frac{d^2n}{dz^2}.$$

In this notation $d\rho^2/dt$ is given by the equation

$$\frac{d\rho^2}{dt}\iiint n\,dx\,dy\,dz = \iiint (x^2+y^2)\frac{dn}{dt}\,dx\,dy\,dz,$$

and it is easy to see that when the above value is substituted for dn/dt, the integral on the right of this equation reduces to $4\mathrm{K}_h\iiint n\,dx\,dy\,dz$.

Hence
$$\mathrm{K}_h = \frac{\mathrm{K}}{1+\omega^2\mathrm{T}^2}.$$

The equations of motion of ions in a magnetic field are usually given in the following form:—

$$\frac{1}{\mathrm{K}}(pu) = -\frac{dp}{dx}+ne\mathrm{H}v, \qquad \frac{1}{\mathrm{K}}(pv) = -\frac{dp}{dy}-ne\mathrm{H}u,$$

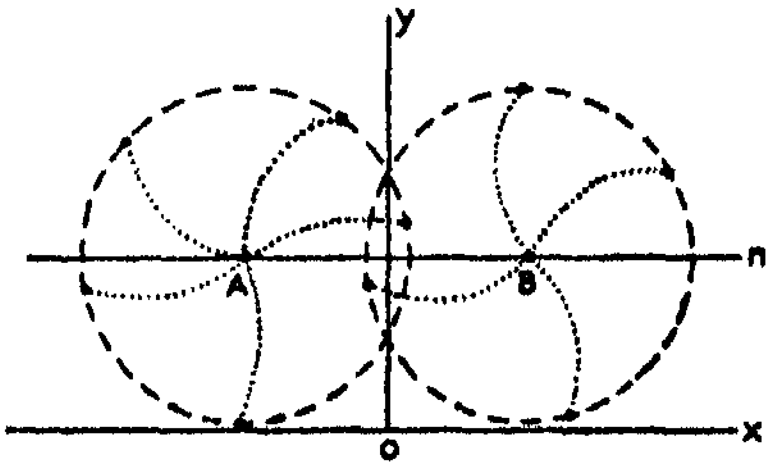
p being the partial pressure of the ions and H the magnetic force in the direction of the axis of z.

These equations are obtained on the supposition that the magnetic force does not affect the rate of diffusion K directly, but acts as if the charge per cubic centimetre ne were moving with velocities u and v. The latter supposition is legitimate for most purposes, since nu represents the excess of the number of ions crossing unit area of the plane $x =$ constant per second in one direction over the number crossing in the opposite direction. The validity of these assumptions when applied to the motion in a magnetic field may be tested by examining the conclusions to which the equations lead in a particular case. On eliminating v, the first equation becomes

$$\frac{1}{\mathrm{K}_h}(pu) = -\frac{dp}{dx}-\frac{\mathrm{H}e\mathrm{T}}{m}\cdot\frac{dp}{dy}.$$

So that when $dp/dx = 0$, there is a velocity parallel to the axis of x due to the slope of pressure dp/dy. Hence, if the surfaces of equal pressure be planes parallel to the plane $y = 0$, there would appear to be more ions crossing the plane $x = 0$ in one direction than in the other.

Let a number of ions begin their paths at a point A and collide with molecules of the gas after traversing a certain distance a from the point at which they started. The points at which they arrive will be situated symmetrically on a circle, and a certain proportion will cross the plane $x = 0$ and collide with molecules on the opposite side. From the point B, at which the number of ions per cubic centimetre is the same as at A, an equal number of ions will start and the same proportion of them will cross the plane $x = 0$ and collide with molecules on the side opposite to B. There will, therefore, be no tendency for the ions to move across the plane $x = 0$ and the only effect of the magnetic force is to cause the ions to move in circular paths, and so shorten their effective mean free paths along the direction of the axes of x and y. Hence $u = 0$ when $dn/dx = 0$. Apparently, therefore, the original equations which lead to an expression for pu involving dp/dy cannot be correct.



4. When ions are moving in an electric field and a magnetic force H is applied along the axis of z, the motion in that direction is unchanged, but in the directions x and y the velocities are altered. Taking the axis of x as the direction of the electric force X, the equations of motion become

$$m\frac{d^2x}{dt^2} = \mathrm{X}e - \mathrm{H}e\frac{dy}{dt}, \qquad m\frac{d^2y}{dt^2} = \mathrm{H}e\frac{dx}{dt},$$

so that the velocities $\dot{x}$ and $\dot{y}$ are given by the equations

$$\dot{x} = \mathrm{A}\sin(\omega t + \alpha) \quad \text{and} \quad \dot{y} = \frac{\mathrm{X}}{\mathrm{H}} - \mathrm{A}\cos(\omega t + \alpha),$$

the velocities at the beginning of the path being $\mathrm{A}\sin\alpha$ and $\mathrm{X}/\mathrm{H} - \mathrm{A}\cos\alpha$. Let $\dot{x}_1$, $\dot{x}_2$, etc., $\dot{y}_1$, $\dot{y}_2$, etc., be the velocities after a number of consecutive collisions of an ion with molecules of the gas.

The distances that an ion travels in the first interval t_1 are

$$\delta x_1 = \frac{\mathrm{A}_1}{\omega}[\cos\alpha_1 - \cos(\omega t_1 + \alpha_1)] \quad \text{and} \quad \delta y_1 = \frac{\mathrm{X}}{\mathrm{H}}t_1 + \frac{\mathrm{A}_1}{\omega}[\sin\alpha_1 - \sin(\omega t_1 + \alpha_1)].$$

The distances traversed in the time $\mathrm{NT} = t_1 + t_2 + \ldots + t_n$ are

$$\Sigma\delta x_s = \frac{\mathrm{NX}}{\mathrm{H}\omega} - \frac{1}{\omega}\Sigma\left(\frac{\mathrm{X}}{\mathrm{H}} - \dot{y}_s\right)\cos\omega t_s + \frac{1}{\omega}\Sigma\dot{x}_s\sin\omega t_s,$$

$$\Sigma\delta y_s = \frac{\mathrm{NXT}}{\mathrm{H}} - \frac{1}{\omega}\Sigma\left(\frac{\mathrm{X}}{\mathrm{H}} - \dot{y}_s\right)\sin\omega t_s - \frac{1}{\omega}\Sigma\dot{x}_s\cos\omega t_s.$$

The terms independent of X obviously vanish in estimating the mean displacements of a group of ions starting from the origin, and the velocities U_h and V_h along the axes become

$$U_h = \frac{\Sigma\delta x_s}{NT} = \frac{X}{H\omega T} - \frac{X}{H\omega NT}\cdot\frac{N}{1+\omega^2T^2} = \frac{X}{H\omega T}\cdot\frac{\omega^2T^2}{1+\omega^2T^2},$$

$$V_h = \frac{\Sigma\delta y_s}{NT} = \frac{X}{H} - \frac{X}{H\omega NT}\cdot\frac{N\omega T}{1+\omega^2T^2} = \frac{X}{H}\cdot\frac{\omega^2T^2}{1+\omega^2T^2};$$

and, since $\omega = He/m$, the expressions for the velocities reduce to

$$U_h = \frac{Xe}{m}\cdot\frac{T}{1+\omega^2T^2} \quad\text{and}\quad V_h = \frac{Xe}{m}\cdot\frac{\omega T^2}{1+\omega^2T^2}.$$

The velocity U when the magnetic force is zero is $\frac{Xe}{m}T$. Hence

$$U_h = \frac{U}{1+\omega^2T^2} \quad\text{and}\quad V_h = U_h\frac{He}{m}T.$$

Also the following relation holds, $U_h/K_h = U/K$, which shows that the velocity in the direction of the electric force is reduced by the magnetic field in the same proportion as the rate of diffusion.

5. The equations of motion from which the number of ions per cubic centimetre at any point in the gas may be determined when electric and magnetic forces are acting are

$$\frac{pu}{K_h} = -\frac{dp}{dx} + nXe, \qquad \frac{pv}{K_h} = -\frac{dp}{dy} + nXe\frac{He}{m}T, \qquad \frac{pw}{K} = -\frac{dp}{dz} + nZe,$$

the component of the electric force along the axis of y being zero.

6. When a stream of ions is moving under the action of an electric force the deflection of the stream from the direction of the electric force may be measured by the ratio

$$\frac{V_h}{U_h} = \frac{He}{m}T = \tan\theta.$$

The deflection varies with the pressure, since T the mean interval between collisions is inversely proportional to the pressure of the gas. Also when e/m is constant the deflection is independent of the electric force.

The value of $\tan\theta$ may be written in various forms, thus

$$\tan\theta = \frac{HU_h}{X}\left(1 + \frac{H^2e^2T^2}{m^2}\right);$$

so that when the deflection is small $\tan\theta = HU_h/X$.

In this case the free paths are only slightly curved by the action of the magnetic force, for the radius r of the circle described by the ion in the plane $z = 0$ is mV/He, and the mean length s of the arc of the circle described between collisions is vT, hence

$$s/r = HeT/m = \tan\theta.$$

The length of the arc s described by the ion is therefore small compared with the radius of the circle.

When θ is large the velocity in the direction of the force becomes

$$U_h = \frac{Xe}{m} \cdot \frac{1}{\omega^2 T} = \frac{Xm}{H^2 e T}, \quad \text{so that} \quad \tan\theta = \frac{HeT}{m} = \frac{X}{HU_h}.$$

In this case the arc of the circle described between two collisions is large compared with the radius.

The velocities of ions U under an electric force in gases at low pressures may thus be easily determined by producing a small deflection θ of a stream with a magnetic force, since $U = U_h$ when θ is small. Also the theory may be tested by observing the effect of a magnetic force on the diffusion of a narrow stream moving under an electric force. In this case when the magnetic force coincides with the electric force, the motion arising from diffusion in directions normal to the force is reduced in the proportion K_h/K, so that the ions are kept together in a narrower stream.

There are several well known phenomena connected with the magnetic rays that occur in discharge tubes, in which remarkable effects are obtained by magnetic forces.

The observed effects are qualitatively in accordance with the above theory, but the conditions under which they are obtained and the system of forces that is called into play are so complicated that an accurate comparison with the theory would not be possible.

A New Treatment of Optical Aberration.

By R. A. Sampson, F.R.S.

(Received March 15,—Read May 23, 1912.)

(Abstract.)

A method is developed by which Gauss's method of relating original and emergent rays in a coaxial optical system

$$\left.\begin{aligned} y &= \beta x + b, \\ z &= \gamma x + c, \end{aligned}\right\} \qquad \left.\begin{aligned} y' &= \beta' x' + b', \\ z' &= \gamma' x' + c', \end{aligned}\right\}$$

by means of a transformation,

$$b' = Gb + H\beta, \quad \beta' = Kb + L\beta, \quad c' = Gc + H\gamma, \quad \gamma' = Kc + L\gamma,$$

where

$$GL - HK = \mu/\mu' = N,$$

may be applied so as to include the aberrations of the third order.

Using $\delta G, \ldots,$ for the added terms for a single surface, of curvature B, with both origins at the tangent plane,

$$G+\delta G = 1+\omega, \quad H+\delta H = \omega/B, \quad K+\delta K = -(1-N)B+B(\psi-\epsilon\omega),$$
$$L+\delta L = N+\psi-\omega,$$

where $\omega = \frac{1}{2}(1-N)B^2(b^2+c^2)$, $\psi = \frac{1}{2}N(\beta'^2+\gamma'^2-\beta^2-\gamma^2)$,

and ϵ is a term which is unity for the sphere and zero for the paraboloid.

It is shown how to build up the values resulting from any series of such aberrations and to obtain finally the aberrational increments $\delta G, \ldots,$ in the forms

$$\delta G = \tfrac{1}{2}\{\delta_1 G(b^2+c^2)+2\delta_2 G(b\beta+c\gamma)+\delta_3 G(\beta^2+\gamma^2)\},$$
$$\delta H = \text{etc.}, \qquad \delta K = \text{etc.}, \qquad \delta L = \text{etc.}$$

The twelve coefficients, $\delta_1 G, \ldots,$ are then shown to obey seven relations, namely,

$$\frac{\delta_2 G-\delta_1 H}{G} = \frac{\delta_3 G-\delta_2 H}{H} = \frac{\delta_2 K-\delta_1 L}{K} = \frac{\delta_3 K-\delta_2 L}{L} = \mathfrak{P},$$

where $\mathfrak{P} = \mu_{-1}\Sigma({\mu_{2r-1}}^{-1}-{\mu_{2r-1}}^{-1})B_{2r}$,

and is in fact Petzval's expression, the vanishing of which is known as the condition for flatness of field in stigmatic systems, and

$$\begin{aligned} \delta_1 N &= G\delta_1 L+L\delta_1 G-H\delta_1 K-K\delta_1 L = K^2 N, \\ \delta_2 N &= \ldots \qquad = KLN, \\ \delta_3 N &= \ldots \qquad = (L^2-1)N. \end{aligned}$$

These lead to Abbe's sine condition, and both throw light on the general relationships of these two well known conditions.

The geometrical interpretation of the presence of the coefficients $\delta_1 G, \ldots,$ at any numerical values, is followed out. The formulæ are then applied, as a numerical illustration, to the calculation of the celebrated Fraunhofer heliometer objective described by Bessel, and calculated with great completeness by A. Steinheil.* In this portion the whole numerical work is given, and it is shown to amount to a mere fraction of that requisite for the trigonometrical calculation as employed, *e.g.*, by Steinheil. Comparison is made with the whole of Steinheil's results, for rays which meet and which do not meet the axis; the numbers are shown to agree within a few units in the last places, and this discrepancy is probably to be attributed to the large number of operations requisite for the trigonometrical calculation. Thus the method is adequate for the numerical calculation of telescopic objectives, and offers a remarkable economy in the work hitherto necessary.

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* 'Munich. Akad. Math. Phys. Class. Sitzungsber.,' vol. 19, Part 3.

The Critical Constants and Orthobaric Densities of Xenon.

By Hubert Sutton Patterson, B.Sc., Richard Stafford Cripps and Robert Whytlaw-Gray.

(Communicated by Sir W. Ramsay, K.C.B., F.R.S. Received March 4,—Read March 21, 1912.)

Rudorf, in a paper on the rare gases and the equation of state,[*] has drawn attention to the high value found by Ramsay and Travers for the density of liquid xenon at its boiling point.[†] As is well known the atomic volume in any group of elements in the periodic table either increases regularly with rise of atomic weight or remains approximately constant, so that it is to be expected that the atomic volume of xenon would be greater than that of krypton, since the value for krypton exceeds that of argon.

If Rudorf's calculated value for the density of neon is taken into account, this anomaly becomes more striking, as is shown from the following table taken from his paper:—

	Neon.	Argon.	Krypton.	Xenon.
Density	1·24	1·404	2·196	3·58
Atomic volume	16·1	28·4	37·8	36·6

According to Rudorf the density of xenon near its boiling point should be 2·68, which would lead to an atomic volume of 48·8, but this question can only be settled by fresh experimental evidence.

For other reasons a study of the densities of liquid xenon and its saturated vapour appeared to us of interest, for the critical volume of this substance has never been determined, and at the commencement of this work the validity of Cailletet and Mathias's law of rectilinear diameters had never been tested with any of the argon series of gases. It might be expected that these gases on account of the simple structure and non-valent character of their molecules would approximate closely in behaviour to the requirements of the kinetic theory of gases and would follow the equation of van der Waals. This equation gives for the ratio of critical density to theoretical density at critical point the value 2·667, and D. Berthelot has calculated[‡] from Ramsay and Travers' densities of liquefied argon that the ratio for this element lies between 2·62 and 2·71. Rudorf, however, by the use of the data of Baly and Donnan for the liquid densities[*] deduced the value 2·95, which, although slightly greater than the theoretical, is much lower than the corresponding value for gases such as CO_2, N_2O, SO_2, which possess a ratio approximating to 3·6. Sydney Young[†] has shown that for a large number of organic liquids this ratio is nearly constant and differs only slightly from 3·77, and regards this number as characteristic of normal non-associated substances. If, however, it should prove that this ratio for the monatomic gases is markedly lower than that for polyatomic gases and vapours, an interesting light would be thrown on the question of molecular association in the liquid state and it would lend support to the view which has often been expressed that all normal liquids are partially associated.

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[*] 'Ann. des Phys.,' 1909, vol. 29, p. 751.

[†] 'Phil. Trans.,' 1901, A, vol. 197, p. 74.

[‡] 'Journ. de Phys.,' III, 1901, vol. 10, p. 611.

These considerations made us anxious to revise the critical constants of xenon and to determine its orthobaric densities; and the kindness of Sir William Ramsay in willingly placing at our disposal the whole of his stock of this very precious gas has enabled us to carry out the measurements with highly purified material and with quantities sufficient to ensure a fair degree of accuracy in the results.

Experimental.—The original determinations of the density and critical constants were carried out by Ramsay and Travers with only about 3 c.c. of gas measured at normal temperature and pressure, and this quantity when liquefied yielded a volume of liquid in the neighbourhood of its boiling point of only 6 cu. mm.

In consequence the xenon could not be effectively purified by fractionation and in their paper the authors claim for their measurements no high degree of accuracy. The specimen of gas investigated by us was originally obtained by Ramsay and Moore[‡] from the residues of about 120 tons of liquid air presented to them by M. Claude, of Paris. The gas after careful fractionation was employed by Moore[§] in the determination of the exact atomic weight of xenon. The xenon, which was of a volume of about 120 c.c. at normal temperature and pressure, was, when it came into our hands, in a high state of purity, but in order to obtain a specimen completely free from possible traces of krypton and air, the whole amount was first solidified in a bulb of small volume and a small amount of uncondensable gas which was present was removed by means of a mercury pump. The remaining gas was surrounded by a bath of cooled pentane,

[*] 'Journ. Chem. Soc.,' 1902, vol. 81, p. 907.

[†] 'Phil. Mag.,' 1900.

[‡] 'Roy. Soc. Proc.,' 1908, vol. 81, p. 195.

[§] 'Trans. Chem. Soc.,' 1908, vol. 93, p. 2182.

the liquid xenon allowed to boil away, and the last fraction, consisting of about 20 c.c., was collected for these measurements. The densities of liquid and vapour were measured in a graduated capillary tube A of approximately 1 mm. internal diameter closed at one end and sealed at the other on to a wider tube B which served as a reservoir for the gas. The capillary carried a nut C by means of which the tube could be screwed into position on a modified Andrews apparatus. The capillary was very carefully calibrated by means of mercury before it was sealed up and the end where the readings of the liquid were taken was specially studied. The form of the tube and the method of filling is best followed from the diagram.

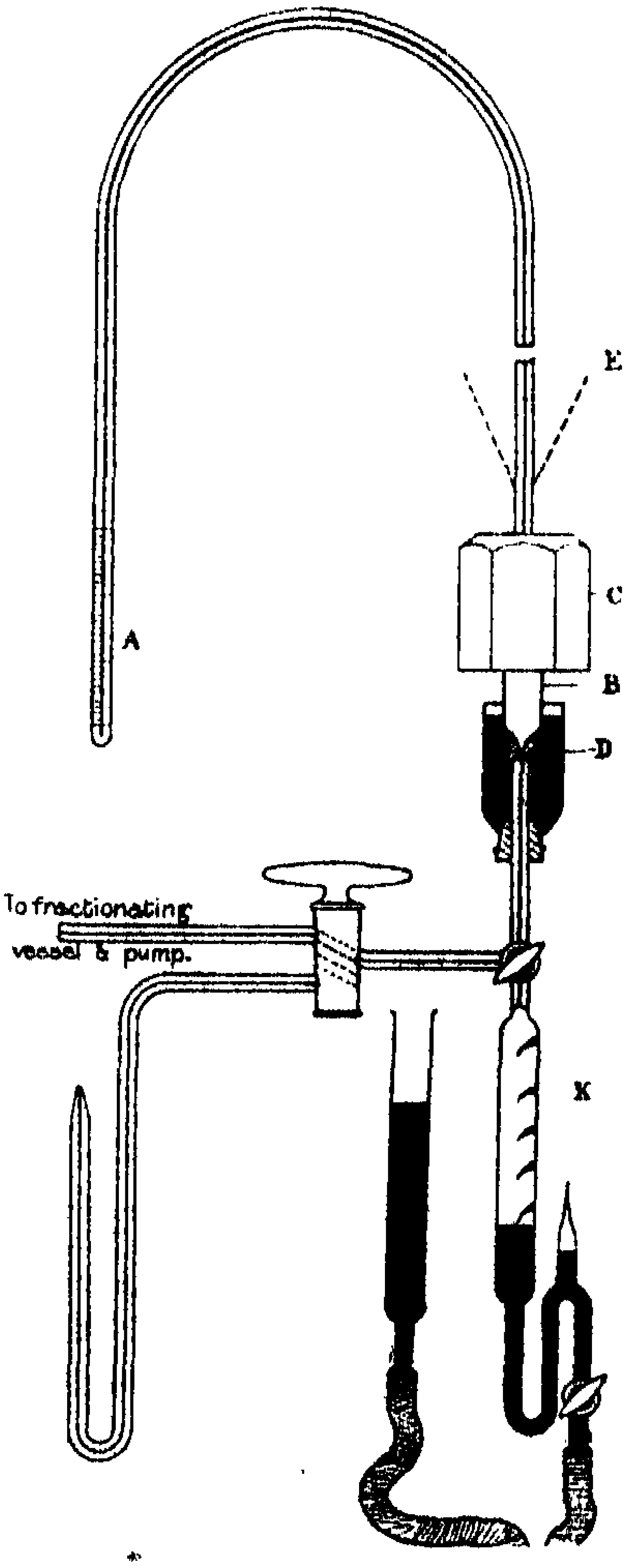

FIG. 1.

The solid xenon, contained in a small fractionating vessel (not shown), was allowed to flow into the perfectly dry and air-free experimental tube AB and was re-condensed again, thus washing out the calibrated tube and its connections. This washing was repeated many times before each filling.

In order to fill the tube, the end A was cooled by immersion in liquid air until sufficient xenon had solidified in it, and a very complete exhaustion was then carried out with the Töpler pump. At the end of this operation, the solid xenon in the capillary was allowed to liquefy and some allowed to boil away into the pump, whence it could afterwards be collected. Finally, A was again cooled, the reservoir B completely filled with mercury to a point E on the capillary, and the mercury thread was frozen by surrounding the tube below E with a paper vessel filled with solid CO_2. The nut and experimental tube were then disconnected at the rubber connection D from the rest of the apparatus and transferred to the compression apparatus. We found all these precautions were absolutely necessary in order to fill the tube with gas which should afterwards liquefy completely at constant pressure. After the measurements of density had been made, the mercury was again frozen at E, the tube detached from the Andrews apparatus and re-connected with the filling apparatus. The gas was pumped off and introduced into the point burette K where its volume was measured. The actual method of reading the volumes of liquid and vapour in the experimental tube was that used by Sydney Young.* At each temperature, readings of the liquid and vapour were taken at four different volumes, and from these data the volumes of vapour yielded by a given volume of liquid were calculated.

The constancy of these ratios was taken as a criterion of the purity of the gas and of the accuracy of the measurements. From these ratios and the known volume of gas in the experimental tube the densities of liquid and vapour were afterwards calculated. In determining the orthobaric volumes by this method it is essential that the volume of the experimental tube containing liquid and vapour shall remain constant for a long enough interval to ensure the attainment of equilibrium between the liquid and gaseous phases and between the temperature of the tube and the bath in which it is immersed. In order to obviate slow changes in volume produced by the change of temperature of the mercury in the Andrews apparatus, we adopted the expedient of keeping the mercury in the capillary tube frozen at E during the readings. Since four readings were made at each temperature, this procedure necessitated thawing and re-freezing the mercury each time the volume was changed, but this disadvantage was more than compensated by the increased accuracy of the readings.

Measurements were made at temperatures ranging from 16° to −66° C. Above 0° the tube was immersed in water contained in a silvered Dewar vacuum vessel, and the temperature was adjusted from time to time by the addition of small fragments of ice. The bath was stirred by means of a stream of air which had previously been cooled, and no difficulty was experienced in keeping the temperature constant to within 0·02°.

Below 0° a bath of alcohol cooled by the addition of small pieces of solid carbon dioxide was used. The higher temperatures were read by means of a standard mercury thermometer, and for temperatures below −20° a pentane thermometer graduated in tenths of a degree, which had been compared with a pentane thermometer standardised at the National Physical Laboratory, and kindly lent us by Prof. Trouton, was employed. The difficulty of maintaining the temperature of the bath constant when working below −30° was overcome by stirring with a stream of air cooled by a mixture of solid carbon dioxide and alcohol. The uncertainty of these temperature readings did not exceed 0·1° C. The results which are given in the following table refer to two separate fillings of the tube, which yielded, however, for the densities at 0° values falling within the limits of experimental error. The total volume of xenon used measured at normal temperature and pressure 16·79 c.c. and 8·752 c.c. in the two cases. The densities of liquid and vapour are expressed in grammes per cubic centimetre, and are therefore in terms of the density of water at 4°. In calculating the results, corrections were applied for the errors of the thermometers, the variation of the volume of the tube with temperature, and for the forms of the meniscus of liquid and mercury.

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* 'Trans. Chem. Soc.,' 1893, vol. 63, p. 1199.

Orthobaric Densities of Xenon.

Temperature.	Vapour density.	Liquid density.	Mean density observed.	Liquid and vapour calculated.	Δ × 1000 obs. − calc.
°	grm. per c.c.	grm. per c.c.			
16	0·844	1·468	1·156	1·156	0
15	0·779	1·528	1·158	1·159	−1
14	0·740	1·592	1·166	1·162	+4
12	0·662	1·677	1·169	1·168	+1
10	0·602	1·750	1·176	1·174	+2
5	0·501	1·879	1·190	1·190	0
0	0·421	1·987	1·204	1·205	−1
−5	0·363	2·074	1·219	1·220	−1
−10	0·313	2·169	1·241	1·236	+5
−20·25	0·235	2·297	1·266	1·267	−1
−30·3	0·180	2·411	1·296	1·298	−2
−39·3	0·139	2·506	1·323	1·325	−2
−49·2	0·103	2·605	1·354	1·355	−1
−59·3	0·078	2·694	1·386	1·386	0
−66·8	0·059	2·763	1·411	1·409	+2

The observed mean densities of liquid and saturated vapour when plotted against the temperature were found to lie very nearly on a straight line. Taking a mean value of all the data, the equation to this straight line is expressed by the formula

$$D_t = 1·205 - 0·003055t,$$

when D_t is the mean density and t is the temperature in degrees centigrade. Hence, between these limits of temperature, xenon follows Cailletet and Mathias's law of rectilinear diameters.

Critical Temperature and Pressure.—Direct readings of the critical temperature were made on several samples of the gas in the compression apparatus, using the method of Sydney Young. The value finally obtained, and which has been confirmed by later measurements, was 16·6°. This is distinctly higher than the original value of Ramsay and Travers, viz., 14·75°. For the critical pressure, readings were taken on the critical isothermal, and the pressures observed were plotted on a diagram against the volumes. The point at which the flexure of the curve changes its sign was taken as corresponding to the critical pressure. The value found was 44·27 metres or 58·2 atmospheres.

Critical Volume.—Knowing the critical temperature, the critical density was calculated by means of the equation already cited, on the assumption that the diameter was strictly rectilinear. It proved to be 1·155 grm. per cubic centimetre, corresponding to a critical volume of 0·866 c.c. per gramme. Xenon has therefore a smaller critical volume and a greater critical density than any other substance so far investigated. Immediately above the critical temperature gaseous xenon is heavier than water.

Vapour Pressures.—A few measurements of the vapour pressures of the liquefied gas were made, but the complete vapour pressure curve has not been determined.

Experiments on this point are in progress. The results obtained are:—

Temperature.	Vapour pressure.
°	metres.
10	38·702
0	31·360
−10	25·246
−20	19·056

From these data the boiling point of xenon has been calculated by the method of Ramsay and Young. The ratios of the temperatures at which xenon and methyl alcohol have the same vapour pressure were plotted against the corresponding temperatures of methyl alcohol. The four points were found to lie nearly on a straight line, and by extrapolation the value of the ratio at the boiling-point of methyl alcohol was obtained, and the boiling-point of xenon calculated from it. The value found for the boiling-point was −106·9° C., which, like the critical point, is higher than the value −109·1° found by Ramsay and Travers, but on account of the somewhat large extrapolation and the small number of points, we regard this figure as only approximately correct.

The mean density at the boiling point of liquefied xenon can be calculated approximately if, as seems probable, the diameter is straight between −66·8° and −106·9°. The value so obtained is 1·538. The density of the saturated vapour, given with sufficient accuracy by assuming the normal coefficient of expansion is 0·013. Hence the liquid density at the boiling point = 1·538 × 2 − 0·013 = 3·063 grm. per cubic centimetre, and the atomic volume of xenon = 130·7/3·063 = 42·7.

Although these values are somewhat different than those calculated by Rudorf for this element, they show that in the argon series there is not only a steady increase in liquid density, but also a progressive rise in atomic volume, with rise in atomic weight, as can be seen in fig. 2.

A study of the equation of the rectilinear diameter shows that the variation in the mean density of liquid and saturated vapour with change of temperature is for xenon remarkably large. For most substances the angular coefficient lies between −0·0023 and −0·0005.*

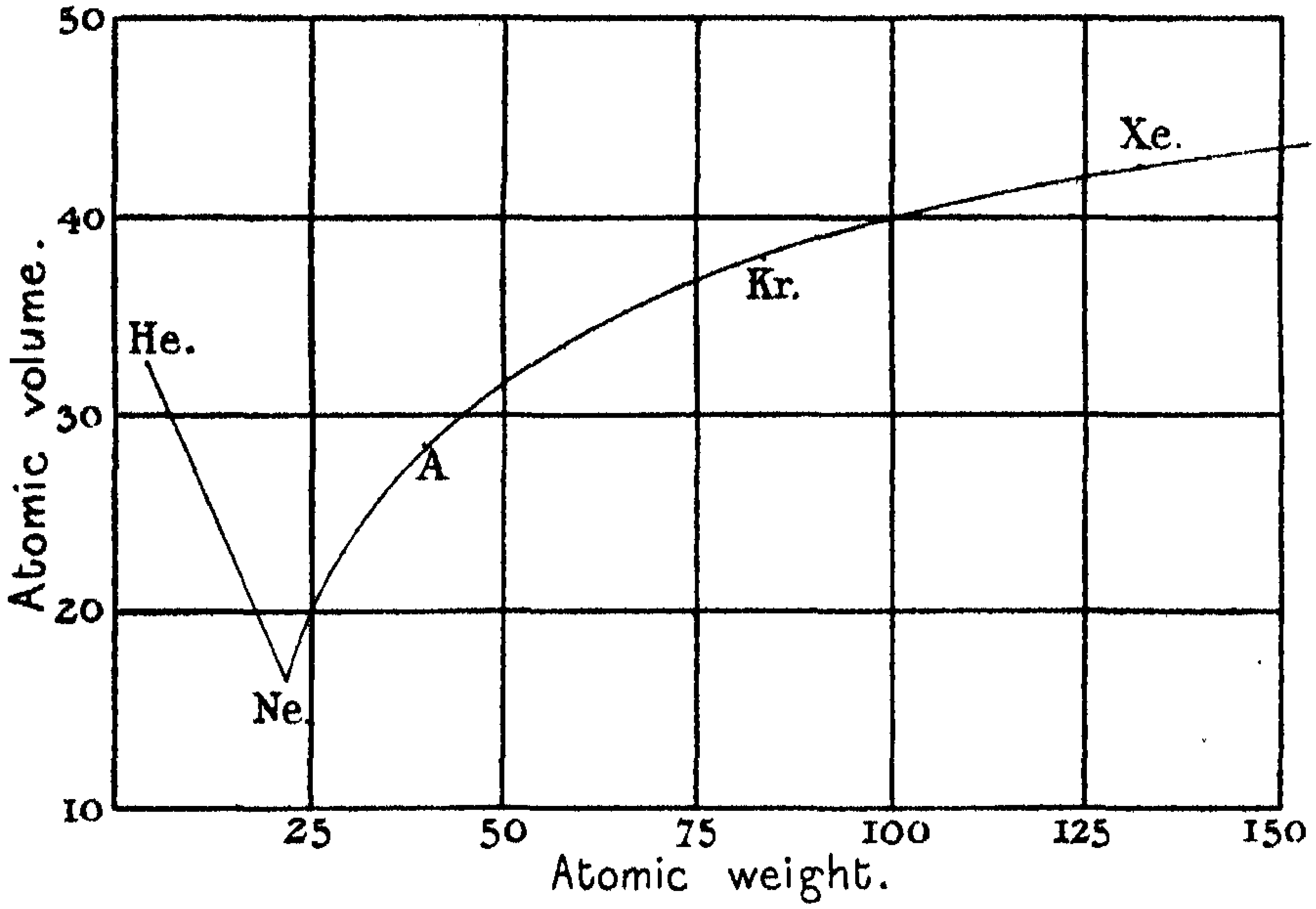

Fig. 2.

Recently, Kamerlingh Onnes and Crommelin have drawn attention to the singularly large coefficient possessed by argon,† viz., −0·003050. The correspondence between this number and our own is striking. The diameters of argon and xenon have not only an almost identical slope, but the slope is greater than that of nearly every substance so far investigated.

The angular coefficient of the helium diameter has been deduced by Onnes from his experiments at very low temperatures on the liquefied gas, and found to be −0·0033, a number not very far removed from that of xenon or argon. A large angular coefficient would appear to be a characteristic of the rectilinear diameters of the rare gases.

Mathias has pointed out‡ that, if van der Waals' law of corresponding states were strictly true for the orthobaric densities of liquid and vapour, the expression $-\theta\alpha/\Delta = a$, where θ = critical temperature in degrees abs., Δ = critical density, α = angular coefficient of inclination of the diameter a = constant, should be the same for all substances.

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* Mathias, 'Le Point Critique des Corps Purs,' pp. 9 and 10.

† 'Proc. Roy. Acad. Amsterdam,' 1911, vol. 13, p. 1020.

‡ 'Mémoires de la Société Royale des Sciences de Liège,' 1899, 3rd ser., vol. 2.

In reality, a is not a constant, but varies for different substances from 0·68 in the case of nitrogen to 1·09 in the case of ethylene.

For argon, Onnes and Crommelin found a = 0·9027; our results for xenon give a = 0·766; so that, viewed from this standpoint, the inactive gases show no greater regularity than the common gases.

The ratio RT_k/p_kV_k or so-called critical coefficient for xenon, calculated from our data, is 3·605, and is hence considerably greater than the value 8/3 = 2·667, which is required by van der Waals' equation.*

This ratio appears to depend on the weight of the molecule, and also on the critical temperature; for substances of low critical point and small molecular weight the critical coefficient is small, whilst Young found that, for the majority of organic liquids he investigated, the ratio approximated to 3·77. If liquefied xenon does not appreciably differ from the majority of liquids in molecular complexity, one would expect its coefficient to exceed that possessed by other gases of smaller molecular weight, as long as their critical temperatures were not far removed from each other. This is exactly what we find, as the following data show:—

	θ.	RT_k/p_kV_k.
	°	
Ethylene	284	3·42
Carbon dioxide	304·3	3·59
*Ethane	305	3·55
Xenon	289·6	3·60

* Kuenen and Robson, 'Phil. Mag.,' 1902, vol. 3, p. 022.

For helium and argon, Kamerlingh Onnes has recently found the values

Helium, 3·13; Argon, 3·283;

whilst for oxygen the value 3·346 was obtained. This constant therefore furnishes no evidence that the elements of the argon series in liquid state are less associated or are simpler in molecular aggregation than any other normal liquids.

Appendix.—The value of these experiments depends mainly on the degree of purity of the xenon, and, before concluding, we wish to draw attention to some curious effects noticed during the research, and which led us at first to suspect that the gas was slightly contaminated. The first specimen of xenon with which the densities were determined was purified in the manner described already. The gas, when compressed in the Andrews apparatus below its critical temperature, liquefied completely without measurable rise of pressure, and, on increasing the volume again, a given volume of liquid always yielded the same volume of vapour, provided the temperature remained constant. The xenon behaved, in fact, like a very pure liquid free from uncondensable gas.

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* Kuenen, 'Die Zustandsgleichung,' p. 60.

Before filling the tube a second time, the gas was passed over heated copper oxide, and then over hot lead chromate, and finally treated with solid caustic potash, with the object of removing possible traces of organic impurities. On liquefaction, unsatisfactory results were obtained, and, when the total space confining the two phases was changed, the volume of vapour yielded by a given volume of liquid was found to vary in different points of the tube.

The xenon was next sparked with oxygen, treated with solid caustic potash, and solidified by cooling to the temperature of liquid air. The oxygen was then removed by pumping, and the gas introduced into the compression tube again. The results obtained were even less satisfactory than before, although no trace of uncondensable gas could be detected. Much time was spent in trying to find an explanation of this behaviour; the experimental tube was re-calibrated, the constant temperature bath was carefully tested, but no source of error could be discovered. The old experimental tube was then replaced by a new carefully calibrated tube, without any change in the results. Experiments were next undertaken to see if the density of xenon at pressures in the neighbourhood of atmospheric was altered by treatment with oxygen. It seemed just possible that a compound between oxygen and the gas might be formed, which at high pressure condensed along with the xenon itself in the experimental tube, and which was the cause of the discrepant results. A large number of experiments were made, with the object of detecting this possible combination, but no convincing evidence of the existence of an oxide was obtained.

The method employed was as follows: A mixture of oxygen and xenon was treated in various ways, viz., sparked at ordinary temperatures, submitted to the silent electric discharge, sparked at a low temperature, etc. The xenon was then solidified by means of liquid air, and the oxygen, which under these conditions remains in the gaseous state, was removed by careful and prolonged evacuation with the Töpler pump. The xenon was finally allowed to gasify, and its density determined in a bulb of about 7 c.c. capacity.

Appended is a short summary of the results we obtained:—

Experiment.		Weight of 1 c.c. of gas at 0° and 760 mm.	
		grm.	
I	Xe and O_2 submitted to silent electric discharge and afterwards cooled to −80°	0·00564	
II	Xe and O_2 sparked at ordinary temperatures	0·00573	Mean of three results.
III	Large quantity of mixture Xe and O_2 sparked and xenon afterwards fractionated	0·00573 0·00567	(1st fraction). (8th fraction).
IV	O_2 liquefied and agitated with solid xenon. Oxygen then pumped off as before	0·00581	
V	Xe and O_2 sparked at −80° in special bulb. Xe solidified, oxygen pumped off and density of remaining gas taken at −80°	0·00597	These results are corrected from −80° C. to 0° C., and hence are not strictly comparable with foregoing.
	Xenon alone subjected to same treatment	0·00592	

Since in these experiments the total volume of gas weighed hardly exceeded 7 c.c. it seemed important to check the method by determining the density of pure xenon in the same apparatus. To obtain the pure gas the xenon was mixed with a small quantity of pure hydrogen obtained from palladium, sparked, dried, condensed, and the hydrogen removed by pumping.

Three density determinations were made, and the values agreed within the limits of experimental error with the value found by Moore:—

Experiment.	Weight of 1 c.c. at 0° and 760 mm.
I	0·00585
II	0·00585
III	0·00586
Mean	0·005854
Moore's value	0·005842

It is hence apparent that the density of xenon is normal after sparking with hydrogen, but in every case after sparking with oxygen, with the exception of Experiment V, too low a density was obtained. It is to be especially noted that Experiment IV, in which the oxygen was merely liquefied and not sparked with the xenon, yielded a nearly normal result. The low values might be caused by the incomplete removal of oxygen from the mixture, but in nearly all the experiments a considerable proportion of the xenon was allowed to escape after the oxygen had been pumped away and before the density was taken.

It is difficult to believe that the solidified gas after this treatment retained as much as 4 to 5 per cent. of free oxygen. Moreover, Experiment IV demonstrates that the mixed gases can be satisfactorily separated by this treatment if the sparking is omitted. Further, in Experiment III, where the mixture was fractionated after sparking, the eighth fraction was distinctly less dense than the first fraction.

The presence of small quantities of ozone in the gas would also account for the low densities, but the precaution was taken of always passing the gas over mercury after sparking and before it was solidified. Moreover, liquid ozone has a deep blue colour, and small traces would be sufficient to tint the solidified xenon. In all the experiments the solid xenon was perfectly white in colour.

On the other hand, it was repeatedly noticed that when the xenon which had been used for the density measurements was collected through the pump and re-solidified it did not completely re-condense, and small quantities of nearly pure oxygen could be pumped off it. It was never found possible, however, by repeated condensations and evacuation to obtain a gas which behaved normally when compressed in the Andrews apparatus. We frequently re-condensed the gas five times, and finally solidified it in the end of the experimental tube, the Töpler pump being kept in constant operation, without obtaining a satisfactory filling. When, however, xenon which had been sparked with hydrogen underwent the same treatment, the gas on compression gave fairly consistent and normal results, as the following figures for the volume of vapour yielded by unit volume of liquid at 0° show:—

After sparking with oxygen......	4·66, 4·76, 4·91.	Mean, 4·78
„ „ hydrogen...	4·58, 4·60, 4·63.	Mean, 4·60

It will be noticed that after sparking with oxygen, the greatest variation is 2·7 per cent. of mean value, whilst the variation after sparking with hydrogen is only 0·65 per cent. It is also noticeable that the mean value is different in the two cases. A similar difference was also observed in the critical temperatures of the two specimens of gas. The oxygenated samples became critical at temperatures varying from 16·9° to 17·2°, whilst the pure gas had a constant critical temperature of 16·6°.

We think it must be admitted that the presence of a small quantity of free oxygen in the xenon would not explain the results. The supposition that small amounts of ozone were present seems at first sight more likely, but does not bear examination, for, apart from the reasons given already, it is hard to see how ozone could have escaped decomposition on standing for days together at high pressure in the presence of mercury in the Andrews apparatus.

On the other hand, if we suppose that an oxide is formed, it is clear that it must be a compound of great instability, and from Experiment V it appears to be more readily formed at low than at high temperature. By sparking at ordinary temperatures, a small percentage of oxide might be produced, which might decompose again fairly rapidly on standing, and by cooling its velocity of decomposition might be greatly diminished as well as its velocity of formation. Since xenon is monatomic, the density of any possible oxide must exceed that of the pure gas, and on this hypothesis the decomposition of the greater part of the oxide during the manipulations involved in a determination would be regarded as the cause of the low densities. It is not improbable, however, that we have here to do with an association of two elements which is essentially physical rather than chemical, and is more allied to absorption or solution than to chemical combination. Such a view is supported by the well-known fact that the inactive gases are slowly absorbed by the electrodes in a Plücker tube when the discharge is passed for a long period, and also by the recent experiments of Claude,* and Ramsay and Collie, who found that on passing a discharge between copper electrodes in an atmosphere of helium and neon, the volatilised metal deposited in the tube contained a large quantity of helium together with a little neon.

Although the experiments just described yielded no definite results they show how oxygen can associate itself with xenon in such a way that the presence of the less condensable gas almost escapes detection. Also these observations showed how the pure gas could be obtained and furnish additional proof of the homogeneity of the xenon employed for the critical constants and orthobaric densities.

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* 'Comptes Rendus,' 1911, vol. 153, p. 713.

On the Observed Variations in the Temperature Coefficients of a Precision Balance.

By J. J. MANLEY, Hon. M.A. Oxon., Daubeny Curator, Magdalen College, Oxford.

(Communicated by Prof. E. B. Elliott, F.R.S. Received March 8,—Read April 25, 1912.)

Introductory.—In a former paper* communicated to the Royal Society, the apparent abnormal behaviour of certain precision balances was described and discussed. One of the most important points therein considered was that dealing with the displacement of the resting-point, R.P., of a beam, consequent upon a uniform rise or fall in the temperature of the instrument. The magnitude of the displacement of the resting-point, R.P., for a change of 1° C. was termed the *temperature coefficient of a balance.*

The variations in the R.Ps. of the balances tested were observed within a somewhat limited range of temperature only. Within those limits they were found to be regular and expressible by an equation of the form

$$R_t = R_s\{1 \pm \alpha t \pm \beta t^2\},$$

in which R_s and R_t are the R.Ps. at some standard temperature and $t°$ respectively, and α and β experimentally determined constants for a given balance and particular load.

In this present communication the author would direct attention to the hitherto unrecorded changes which may occur in the temperature coefficients of delicate balances, and offer some further remarks upon the subject in general.

Description of Balance.—The balance used during this investigation was obtained new, direct from the makers, Messrs. A. Gallenkamp and Co., about three years ago. The beam is cantilever in type and enclosed by an inner protecting case, as recommended in my former paper. As the result of prolonged testing, I conclude that the balance fully merits the distinction which the makers claim for it, namely, a practically constant sensibility for all loads varying from 0 to 200 grm., this latter being the maximum load for which the balance was built. The sensibility of the balance was, with advantage, set somewhat high, and equal to 45 divisions per 1 mgrm.; its value was kept unchanged throughout. The equality of the temperature of the beam could at any time be tested by means of a differential bolometer placed within the beam case, and capable of indicating so small a difference as 1/10,000° C. As the bolometer was fully described in my former paper an account of it here is unnecessary.

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* 'Phil. Trans.,' A, vol. 210, p. 387.

Experimental Work.—The temperature coefficient was, in the first instance, calculated from data obtained during March, 1909, the range in the temperature during the observations being from 10° to 16° C. The accompanying graphs (fig. 1) illustrate the variations which at that time occurred in the R.P. as the temperature, or load, or both were altered.

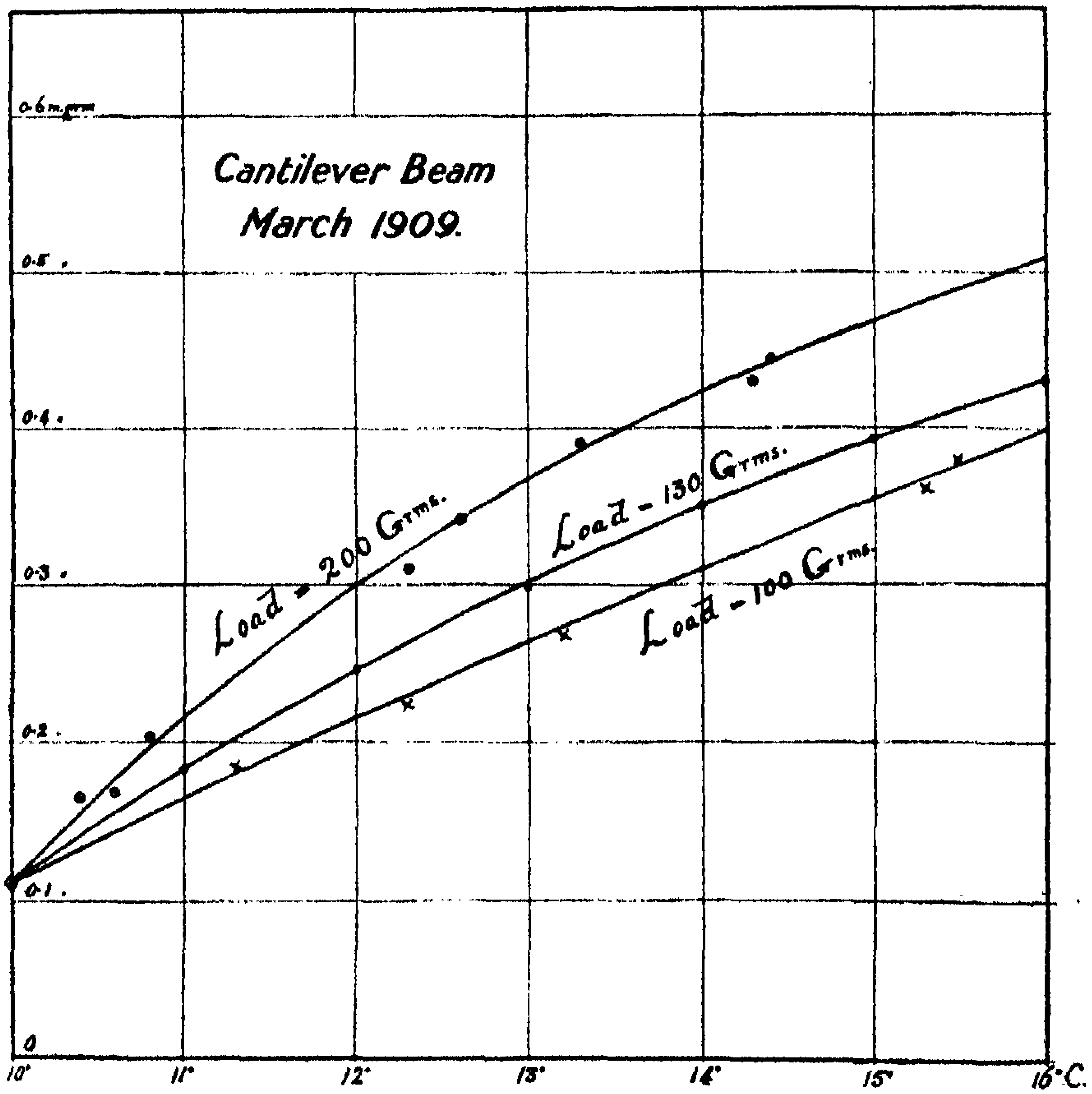

FIG. 1.

As the variations in the R.P. with changes in the temperature and load were found within the above-named limits of temperature to be both definite and regular, the conclusion was drawn that for a small additional range, the application of the method of extrapolation might be resorted to with a sufficient degree of safety. This course was therefore adopted for reducing to a standard temperature a series of weighings, some of which had been carried out when the temperature of the balance room approached 18° C. It was then seen that, whilst the weighings at temperatures up to and including those at 16° C. were, when reduced, very concordant, those made when the temperature approximated 18° C. gave, when corrected and compared with the values obtained at the lower temperatures, inharmonious and variable values.

With the object of elucidating the cause of these discordant values, each pan of the balance was loaded with 130 grm., this load being practically equal to that of the substances which were being weighed when the discrepancies were detected. Taking the precautions shown to be necessary and described in my former paper, a number of observations of the R.P. were made at temperatures ranging from 16° to 21·6° C., during August 1, 3, and 4, 1910. The different values then found for the R.P. are plotted against the corresponding temperatures and shown graphically in fig. 2.

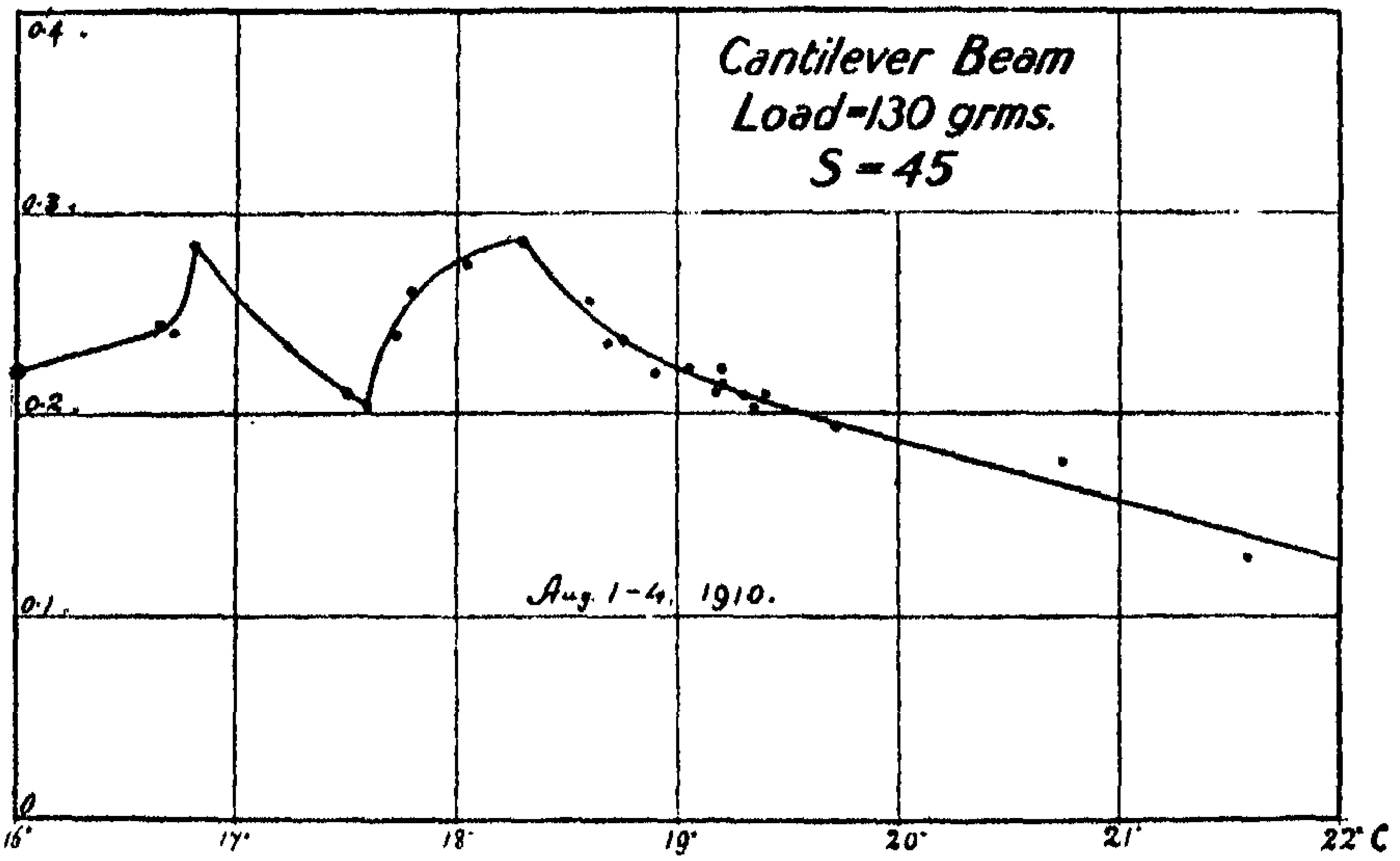

Fig. 2.

Here it may be seen that the regularity which exists in the temperature coefficient curve up to 16·7° C., or thereabout, suddenly disappears; between that temperature and 19·0° C. the beam is, with reference to its temperature coefficient, in a state of unstable equilibrium. We have here a well-marked example of what I venture to term a *critical temperature range* for this particular balance and load.

Referring again to the curve (fig. 2) we observe that for temperatures above 19·0° C. the coefficient k again becomes well defined and regular; but its former positive value has now given place to another and negative value.

Therefore, if an object is weighed when the temperature is below 16° C., its weight will appear to *increase* as the temperature of the balance approaches the limit, 16° C. Similarly, there will be an apparent *decrease* in the mass of the same body when it is weighed after the temperature has passed beyond the upper limit, 19·0° C. All weighings taken when the temperature falls within those two limits will yield more or less uncertain values.

Having completed the observations just described, the balance was rested for two months, and then a new series of determinations of the R.P. was commenced. These were conducted at intervals during October 4 to 8 inclusive, the temperature of the balance varying within the limits 14·7° and 20·6° C. The results obtained upon this occasion are represented in graph No. I[*] (fig. 3).

The beam was now given the more prolonged rest of 23 weeks, after which a third series of observations was undertaken. These were commenced on March 22, and concluded on March 24, 1911. During that time the temperature of the balance varied within the limits 12·9° and 19·9° C

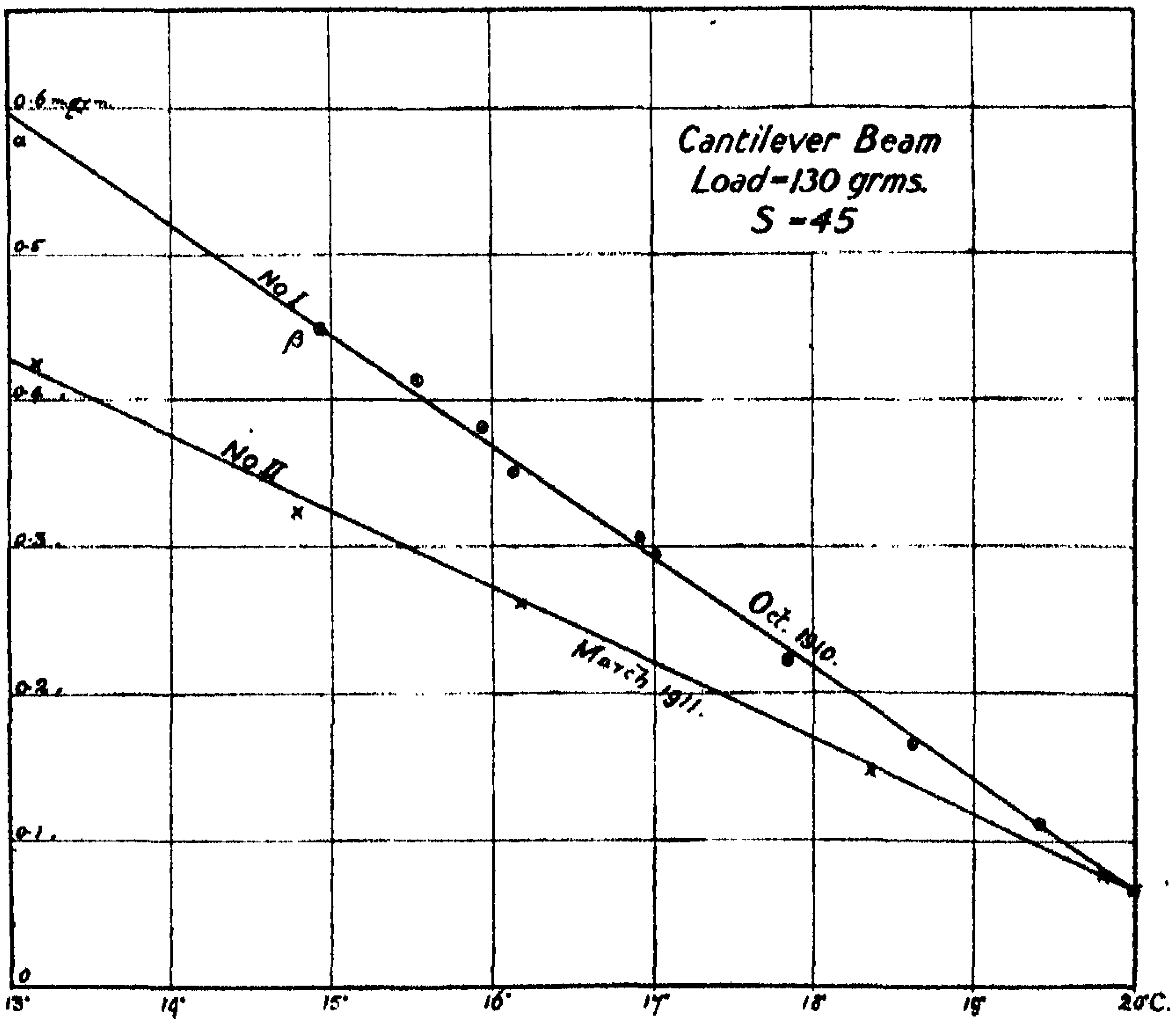

FIG. 3.

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[*] The portion α...β was obtained by extrapolating.

Graph No. 2 (fig. 3) was plotted from the data secured during this last series of experiments. Although the characteristics of the two curves are similar, it will be observed that the slope of No. II is less marked than that of No. I. Comparing these two curves with those given in fig. 1, we also observe that the change from a positive to a negative value is accompanied by a decided simplification in the nature of the curve; and that, whereas formerly the type of the temperature coefficient k was represented by the equation $k = 1+\alpha t-\beta t^2$, it has now, within the experimental limits, become expressible as a straight line equation, namely, $k = 1-\alpha_1 t$.

Since the completion of the third and last series of determinations from which the present value of k was calculated, a very large number of weighings of different objects have been carried out with this balance; the temperature has been allowed to vary quite freely; the maximum temperature was as high as 23·4° C. in August, and the minimum as low as 10·4° C. in October, 1911. During the past ten months the temperature coefficient k appears to have remained strictly constant; the values obtained from numerous weighings of the several bodies at different temperatures having shown, when reduced to a standard temperature of 16° C., a remarkable degree of concordance. With the balance adjusted to so high a degree of sensibility as that already named, it is believed that any further change in k could scarcely have escaped detection.

Discussion.—On a previous occasion* an attempt was made to explain why certain precision balances exhibited a behaviour which was termed anomalous, and the opinion was expressed that the observed and correlated variations in the temperature and R.P. of a beam were primarily due to very small inequalities in the movements of the several groups of screws, together with their associated knife-edge blocks. The additional evidence secured during this and another research not yet concluded, tends to confirm and strengthen this opinion. The probability of the correctness of such a view will, it is believed, be apparent from the following theoretical considerations.

If, when the temperature of the beam is varied, the nature and sum of all the resultant movements of the screws forming one group are precisely equal both with regard to the nature and sum of all the movements of the corresponding screws of an opposed similar group, there will result a small but perfectly symmetrical movement. Such a movement may either lengthen or shorten the two arms of the beam, but will leave the ratio of their lengths unaffected. Therefore, under these conditions, provided the masses of the disturbed parts are strictly equal, the R.P. of the beam will experience no change and the temperature coefficient $k = 0$.

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* 'Phil. Trans.,' A, vol. 210, p. 398.

If, however, the total movement of two opposed groups of screws is unsymmetrical, the final result will be a more or less distinct differential displacement of the one group with reference to the other, and the greater the change in the temperature, the larger will be the differential displacement. Now any perceptible movement of this nature will at once affect the ratio of the two arms and thus cause a shifting of the R.P. This shifting, when it proceeds with uniformity as the temperature increases or decreases, may be determined and its value per 1° C. calculated. A definite expression for the temperature coefficient k is thus obtained; k may be either positive or negative according to the direction in which the R.P. moves as the temperature increases or decreases.

If this mode of accounting for the presence or absence of the temperature coefficient of a balance be rejected then it would appear that there still remain two alternatives.

1. It may be suggested that the variations in the R.P. are caused by slight differences in the flexure of the two arms as the temperature varies. In my former paper it was shown that this view is incorrect, for in no investigated case was there found any measurable difference in the flexure of the two arms when the temperature or load, or both, are varied. Further, the balance used during this present research maintained an unchanged sensibility for all loads; this would have been an impossibility had the beam suffered either equal or differential flexures.

2. The remaining alternative assumes the possession by the beam of distinctly different coefficients of expansion for the two arms. It is, however, well known that in the case of first-class precision balances, very great care is exercised both in preparing and selecting only such alloys, the physical characteristics of which suggest a highly homogeneous whole; and, therefore, any conclusion based upon the assumption of the presence of irregularities in the coefficient of expansion of the beam would appear to be not only unwarranted but also untenable.

If these views be accepted, we meet with no insuperable difficulty in accounting for the observed transformation of a positive temperature coefficient into one which possesses a negative and distinctly different value. We proceed to consider this point.

The transient nature of the instability observed in the R.P. of the cantilever beam as the balance was made to pass through the critical temperature range, may to some appear not a little remarkable. But in the author's opinion this behaviour of the beam should cause no surprise. We are here dealing with a balance which had been in use for a comparatively short period; and, therefore, the conditions as to load and temperature had not been sufficiently varied to enable the knife-edges and their kindred parts to take up truly normal positions. For the purpose of removing some slight abnormal strains it was imperative that the beam should be subjected to the combined influences of a certain minimum load and a range of temperature approximately equal to 3° C. above 16·7° C. As soon as those conditions were fulfilled, it appears that some one or more of the parts secured to the beam proper moved into other and slightly different positions; these new positions they still retain. Such slight readjustments in the relative positions of the several screw groups might readily be accompanied by a transference of a major strain from one group to another, and thus, in a perfectly natural manner, bring about the changes observed both in the sign and value of k as cited in the experimental section of this paper and shown graphically in fig. 2.

Some may dissent from the views and conclusions expressed above, but few, if any, will deny the importance of the experimental results which have been obtained during this present research. We therefore pass from points of theoretical interest to a consideration of the manner in which, according to our view, the beam must be "aged."

On the "Ageing" of a Beam.—The marked changes noted in both the character and value of the temperature coefficient of the cantilever beam almost inevitably lead us to conclude that, before a new, or even comparatively new, precision balance can be safely used for securing trustworthy values of the highest order of accuracy, the instrument must be suitably "aged." In making this suggestion nothing novel or unusual is proposed. Every physicist is familiar with the fact that many precision instruments (such as standard resistance coils and thermometers) are incapable of yielding really reliable values before they have been subjected to an "ageing" process of some kind.

It is fortunate that in the case of a balance beam, the ageing can be so conveniently effected.

If the single instance already described can be accepted as a safe criterion, it will appear that the ageing of the beam may be brought about as follows:—

The balance should be first placed in a room having a somewhat lower temperature than that likely to be encountered during the subsequent research; the pans must then be suitably loaded and the beam released. (Possibly the load should be the maximum for which the instrument is built; but experiment alone can enable us to determine this.) After a time the temperature of the room should be gradually increased until it has passed beyond that which is known to be the upper temperature limit. If the R.P. be determined at intervals during the slowly increasing temperature, we at the same time obtain the necessary data for calculating temperature coefficient k of the beam.

By repeating both the process and the observations, we may acquire all the evidence we need for a critical examination of the behaviour of the beam during the whole treatment, and thus be able to determine whether a further ageing of the beam is desirable.

It is quite possible, indeed, we think it is highly probable, that some balances may have to be "aged" for the particular loads they are to carry during the subsequent research. It is conceivable that under the influence of a given stress, one group of screws may manifest, relatively, a large degree of freedom; the application of a totally different stress may cause the larger degree of freedom to be transposed to another group. But it is to be hoped that further experiments will show that such tactics on the part of a balance are the exception rather than the rule.

By referring to the numerous papers dealing with atomic weight and other determinations involving very accurate weighting, we find that investigators have frequently made a special point of securing a new balance for their research. Viewed in the light of the facts we have given, it would appear that this plan might in some cases be productive of uncertain and misleading data. We believe that the most reliable instrument for highly refined weighings is a well-cared-for balance that has been regularly and freely used for at least two or three years. Under those conditions there will be a tendency for the balance to become aged in a perfectly natural manner. The author does not commit himself to the extent of asserting that the artificial ageing process advocated by him is thus rendered wholly unnecessary; on the contrary, he is of opinion that whenever very refined weighings are to be undertaken, the safe plan is to resort to the device for ageing the beam, prior to the inauguration of the research. In this way alone can it be determined whether or not the balance merits that large degree of confidence which we at times are apt to repose in it.

Effects Produced by Sudden Changes in the Temperature of a Balance Shelf.—During the concluding stage of another research, a new and hitherto unobserved disturbing factor recently asserted itself; this factor assumed the form of a diurnal variation in the R.P. On certain days the values of the reduced R.Ps. increased very slightly but steadily as the day advanced; generally, the value attained a maximum by 2 P.M. and then remained, within the limits of experimental error, invariable throughout the afternoon and evening. The cause of this shifting in the R.P. was not at once apparent; but ultimately it was suspected to be due to a minute tilting of the shelf upon which the balance rested, the disturbing element of the tilt being in a direction parallel to the length of the beam. Any tilt imparted to the shelf will obviously be correspondingly shared by the central pillar which supports the beam; and as the summit of the pillar will, for a given tilt, describe a larger arc than the base, it follows that (other conditions remaining constant), the pointer will suffer a lateral displacement with regard to the scale placed behind it; but the actual angular position of the free beam, when referred to a vertical line, will remain unaffected. That this hypothesis was correct was proved in the following way.

A stout-walled glass tube, having a diameter of 25 mm., was chosen; by grinding, one end was adjusted until its plane was very approximately at right angles to the tube's axis; the other end was softened and drawn out, so as to form a short, rigid, capillary tube. A pendulum, consisting of a small brass sphere suspended by a very fine platinum wire, was then introduced, the free end of the wire being passed up through the capillary at the top, and there secured by means of a plug and cement. Immediately behind the wire, and just above the bob, was fixed a strip of Bristol board, with a thin but well-defined vertical index line drawn upon it. The distance from the point of suspension to one end of the index line was practically equal to the distance from the central knife-edge of the balance to the lowest extremity of the pointer. The tube, with its enclosed pendulum, was then set up upon the plate glass slab, upon which the balance stood, and there fastened with a little cement. For the purpose of measuring the distance between the pendulum wire and the index line, use was made of a reading-telescope, placed at a distance of 2 metres, and fitted with a micrometer eye-piece, capable of indicating 0·01 mm. This apparatus afforded all that was required for detecting and measuring those minute lateral displacements of the balance pointer that might be produced when the shelf was tilted. As the balance pointer and the tilt-detecting pendulum were of equal length, by measuring the side displacement of the latter we discover the corresponding movement of the former.

In these experiments no attempt was made to measure any lateral displacements that were less than 0·01 mm.; this was sufficiently small for our purpose, and was therefore accepted as a minor limit. It may be mentioned that a lateral displacement of the pointer amounting to 0·01 mm. was approximately equivalent to 0·002 mgrm.

Experimenting with the above described apparatus, conclusive proof was soon obtained that the daily growth observed in the R.P. was due to slight vertical movements at one or both ends of the balance shelf. These vertical movements never equalled 0·2 mm.; generally, they varied within the limits 0·05 – 0·15 mm. Other experiments revealed the cause. It was found that the disturbances occurred only when the room temperature was varied somewhat *suddenly*. When care was taken to *slowly* vary the temperature, there was no measurable displacement of the pendulum, and reduced R.Ps. were quite normal.

From the evidence here given in brief, it will probably be gathered that, in the author's opinion, the balance shelf possessed a temperature lag sufficient under the given conditions to develop a deformation which was manifested in the manner already described.

We were now in a position to control the disturbing element, and the necessary measures for its complete suppression were accordingly taken. By weighing only after the room temperature had remained nearly constant for some considerable time, all difficulties arising from the cause discussed above have been successfully avoided.

In connection with highly refined weighings, constant use is now made of the tilt indicator. The instrument is permanently placed upon and near one end of the balance shelf, and from the indications which it offers we at once know whether a weighing may be advantageously proceeded with or not.

Appendix.

Since the publication of my former paper, Mr. L. Southerns, of the Cavendish Laboratory, Cambridge, has drawn my attention to some experimentsland observations of his own. In a paper on the "Dependence of Gravity on Temperature,"* he shows that soon after heating the contents of the calorimeter, which was suspended from one arm of his balance, an apparent increase in weight was noted; this apparent increase is attributed to a decrease in the buoyancy of the air immediately surrounding the calorimeter. This view, although correct as far as it goes, is nevertheless incomplete. The ascending warm air would certainly lengthen the balance arm from which the calorimeter was suspended, and therefore the apparent increase in weight was due to the joint effects produced by the decrease in the density of the enveloping air and the change in the ratio of the arms of the beam. Such effects are, as I have already shown, quite distinct from those which properly appertain to and are restricted to the temperature coefficient of a balance. The changes observed by Mr. Southerns could be demonstrated with *any* precision balance, but with *some* balances it would be difficult, if not impossible, to render the possession of a temperature coefficient evident.

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* 'Roy. Soc. Proc.,' A, vol. 78, p. 393.

The General Theory of Colloidal Solutions.

By W. B. Hardy, F.R.S.

(Received March 13,—Read May 16, 1912.)

A large number of observations upon the filterability and the optical properties of colloidal solutions prove that they are coarse grained and consist of particles dispersed throughout a continuous fluid phase. For this reason these solutions are commonly described as multiphase systems in which the dispersed particles form one of the phases. This description is wrong unless it be qualified by the further statement that the particles do not constitute a phase *in esse*, but only a phase *in posse*.

Consider a heterogeneous fluid such as is described above in contact with its own vapour, and let the components be two, *e.g.* gelatine and water. If the fluid really consisted of two phases there would, with the vapour, be three phases. Let us distinguish the vapour phase by v and the exterior and interior fluid (or solid) masses by $''$ and $'$ respectively. Then, since the surface enclosing the interior fluid (or solid) masses is curved, we have

$$p^v = p'' < p'.$$

The variables, therefore, are the two components, temperature, and two pressures, or five in all. Since by hypothesis there are three phases, the system has two degrees of freedom. Therefore, in order completely to define the system, it will be necessary to fix the temperature and one of the pressures, or the composition of the phases. But on this hypothesis the two fluid phases are separated by a curved surface, and this introduces a difficulty; for if the surface be freely permeable by the components the potentials and pressures in the two phases must be the same, and, as neither component is confined to the interior phase or to the interface, that phase is unstable.* The phase rule is applicable only to contiguous masses which are thoroughly stable, whereas the stability of the interior masses in colloidal solutions is open to question. From the fact that the state of the solution at any instant is determined not only by temperature, pressure, and composition, but also by previous history,† we may conclude that neither the exterior nor the interior fluid masses conform to Gibbs' criterion of stability, namely, that the value of the expression $\epsilon - T\phi + Pv - \Sigma Mm$ when ϵ, ϕ, v, m, are respectively intrinsic energy, entropy, volume, and mass, and T, P, and M constants, shall be zero for the particular phase and either zero or positive for any other phase of the same composition.

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* Gibbs, 'Trans. Conn. Acad.,' vol. 3, p. 406.

† In order to obtain comparable results for osmotic pressure or viscosity, it is necessary to start the system from a fixed point and allow it to proceed along a particular path.

"If equilibrium subsists (in such systems) without passive resistance to change it must be in virtue of properties which are peculiar to small masses surrounded by masses of different nature and which are not indicated by the fundamental equation."[*]

There is no intention at this stage of attempting to elaborate a complete theory, and enough has been said in support of the contention that it is almost as erroneous to speak of colloidal fluids as multiphase systems without qualification as it would be to ignore their heterogeneity altogether.

The nature of the problem and the particular questions which need investigation may be brought out by considering a simplified diagrammatic scheme of a system consisting of a heterogeneous fluid in contact with its own vapour. Let it be supposed that a solution of A in B is homogeneous and forms a simple phase when the concentration of A is sufficiently small, but becomes heterogeneous by the separation of small globules rich in A and poor in B when the concentration rises above a point defined by temperature and pressure.[†] It would obviously be possible to produce the required concentration by compressing the mass in a cylinder with a piston permeable only to the solvent B. Let this be carried out and let the system now consist of vapour of B, pure B, and a heterogeneous fluid consisting of a weak solution of A in B, with globules of solution rich in A dispersed through it, and let us agree to distinguish the vapour phase by v, the pure solvent by s, the globules by $'$ and the external solution by $''$. The piston which separates solvent from the complex solution is maintained in position by a force which is obviously equal to the osmotic pressure of the solution. Call this pressure P.

Let the volume of the space under the piston be V, and let there be only one globule present. For a small compression which expels $d\mathrm{V}$ of solvent and causes the globule to increase by dv' we have

$$dv'' = d\mathrm{V} + dv', \tag{1}$$

and, if m_1 be the mass and μ_1 the potential of the solvent, and m_2 and μ_2 the mass and potential of the solute, and t the tension and a the area of the surface of the globule, we have for the thermodynamic potential

$$\begin{aligned}(d\psi)_\theta = & -p^v d\mathrm{V} + p'' dv'' - p' dv' \\ & + \mu_1^s dm_1^s + \mu_1' dm_1' - \mu_1'' dm_1'' + \mu_2' dm_2' - \mu_2'' dm_2'' + d\,(ta),\end{aligned} \tag{2}$$

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[*] Gibbs, *loc. cit.*, p. 159.

[†] **For the limitation of this supposition in connection with infinitesimal changes of state see Gibbs, pp. 187—193.**

an equation which is true only if the specific volumes of the components be reckoned the same throughout the fluid parts of the system.

But if the piston is completely permeable to the solvent, and the surface of the globule is completely permeable to both solvent and solute,[*] we have

$$\left.\begin{aligned} \mu_1^s &= \mu_1' = \mu_1'', \\ \mu_2' &= \mu_2''; \end{aligned}\right\} \tag{3}$$

nd since $$dm^s{}_1 + dm_1' = dm_1'' \quad \text{and} \quad dm_2' = dm_2'', \tag{4}$$

all the terms including these quantities disappear.

Also, if P be the pressure on the piston—that is the osmotic pressure—and P′ be the excess pressure in the interior of the globule due to the tension of the surface, then

$$p'' = \mathrm{P} + p^v \quad \text{and} \quad p' = \mathrm{P}' + p''. \tag{5}$$

Equation (2) now reduces to

$$(d\psi)_\theta = \mathrm{P}d\mathrm{V} - \mathrm{P}'dv' + d(ta).$$

Dividing through by $d\mathrm{V}$, and remembering that $(d\psi/d\mathrm{V})_\theta = \mathrm{P}$, we get

$$\mathrm{P}'dv' = d(ta),$$

and from (5)

$$\mathrm{P} = -t\frac{da}{dv'} - a\frac{dt}{dv'} - p^v + p' = -\frac{2t}{r} - \frac{dt}{dr} - p^v + p'. \tag{6}$$

In colloidal solutions there is usually a difference of electric potential between the globule and the exterior fluid due to polarisation of the interface. The electric density must be a function of the chemical nature and density of the matter on each side of the interface, since the polarisation is due to chemical and osmotic forces acting across it. Therefore, if the globule be so large as to contain in its interior a phase fully formed (that is if the radius be greater than the effective range of any of the molecules there present) the electric density will be sensibly independent of the size of the globule, being, like the pressures and potentials of the interfacial film, fixed by the phases on each side supposed constant. But when the radius is less than the range of molecular action the composition and physical properties of the globule will vary, and therefore the density of the charge on the surface will also vary.

An expression for the energy of an interfacial layer expressed in terms of tensions may be got by the method of Dupré*: "If T_{12} denote the interfacial tension, the energy corresponding to unit of area of the interface is also T_{12}, as we see by considering the introduction (through a fine tube) of one body into the interior of the other. A comparison with another method of generating the interface similar to that previously employed when but one body was in question will now allow us to evaluate T_{12}.

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[*] The latter part of this assumption probably is not true of actual colloidal systems, for if any degree of mechanical stability be imparted to the interface by, *e.g.*, an electric charge, the great difference in diffusibility between solute and solvent (leading to great differences in the rate of transference across the interface) will operate in finite time as though the surface were only partially permeable to the solute.

"The work required to cleave asunder the parts of the first fluid which lie on the two sides of an ideal plane passing through the interior is, per unit of area, $2T_1$, and the free surface produced is two units in area. So for the second fluid the corresponding work is $2T_2$. This having been effected, let us now suppose that each of the units of area of free surface of fluid (1) is allowed to approach normally a unit area of (2) until contact is established. In this process work is gained which we may denote by $4T'_{12}$, $2T'_{12}$ for each pair. On the whole, then, the work expended in producing two units of interface is $2T_1+2T_2-4T'_{12}$, and this, as we have seen, may be equated to $2T_{12}$." Hence

$$T_{12} = T_1+T_2-2T'_{12}.\dagger \qquad (7)$$

Experiments with plane surfaces (see next paper) suggest that the term T'_{12} consists mainly of the electric energy per unit area of interface due to electric polarisation. But as this is not established it will be well to proceed in a more general way.

Let T represent the tension which the interface would have if no polarisation occurred, then putting σ as the electric density on the surface of the globule, we have for t the actual tension

$$t = T-\phi(\sigma), \qquad (8)$$

a relation which implies that the total energy per unit area of interface is fixed by the mass of the components and the temperature. From (6) and (8) we get

$$P = -\frac{2T}{r}-\frac{dT}{dr}+\frac{d\phi(\sigma)}{dr}+\frac{2\phi(\sigma)}{r}-p^v+p'. \qquad (9)$$

As an approximation, the electric displacement at the interface may be represented by two concentric shells, each infinitely thin, and with electric density σ and $-\sigma$. The radius of the inner shell being the radius of the globule r, and the distance between the shells x, the energy due to polarisation is then given by

$$8\pi^2r^4\sigma^2\frac{x}{r(r+x)}.$$

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* Lord Rayleigh, 'Phil. Mag.,' 1890, (5), vol. 30, p. 461.

† Equation (7) is rigorously true, for, if account be taken of any work gained or expended in the formation or condensation of vapour, the balance of such work is zero, if Dalton's law be assumed.

Putting x constant, we have

$$P = -\frac{2T}{r} - \frac{dT}{r} + \frac{8\pi^2 x r^2 \sigma}{r+x}\left[\frac{\sigma(2r+3x)}{r+x} + 2r\frac{d\sigma}{dr}\right] + \frac{16\pi^2 r^2 \sigma x}{r(r+x)} - p'' + p'. \quad (10)$$

If the solute A were an electrolyte, account would have to be taken of the electric work gained or lost in phases ′ and ″ during the compression.*

Equations (9) and (10) show that the osmotic pressure of a schematic colloidal solution such as we are considering depends upon the functions dt/dr and $d\sigma/dr$.

When r exceeds the range of molecular action, the globule contains in its interior a phase (the interior phase) fully formed, but under a pressure greater than the pressure p'' of the external phase by the quantity $P' = 2t/r$. Let us make the probable assumption that, when the globule has grown to this size, so as to constitute a phase in mass, the pressure P' has fallen so low as to cease to affect sensibly the composition or properties of the internal phase.

Since the pressure and potentials of the layer of transition between phases ′ and ″ are fixed when those phases are fixed, dt/dr and $d\sigma/dr$ become equal to zero, and the equation becomes

$$P = -\frac{2t}{r} + \frac{2\phi(\sigma)}{r} - p'' + p'. \quad (9)$$

The point where r is equal to the extreme range of mutual action of any of the molecules present is therefore one of great importance. Three things therefore need discussion: they are the forms of the functions dt/dr and $d\sigma/dr$ and the range of molecular action.

The Surface Tension of the Globule.—Lord Rayleigh† has shown that, according to the Young-Laplace theory of capillarity, the tension of a very thin film of matter should increase as the film thickens, according to the square of the thickness. Experiment with actual films has failed to confirm this generalisation. The experiments of Reinold and Rücker‡ and of Johannot§ prove that, for soap films in air, the curve connecting tension and thickness shows a series of maxima and minima (fig. 1).

The tension in the case under consideration is that of a drop of liquid forming in the interior of a mass of liquid. It is therefore that of a fluid-fluid interface. If, however, the function dt/dr has maxima and minima, certain important conclusions follow. For let phase $''$ be supersaturated with respect to phase $'$: by raising the osmotic pressure P_0 to P_1, the result would be the formation of a globule of tension t_1 and radius r_1. But if the system contains globules of radius $>R$, and the osmotic pressure be reduced by admitting solvent, globules of tension T_2 and radius R_1 will be formed.

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* In order to simplify the problem, any kinetic energy which the globule may possess, owing to progressive motion, has been neglected. This quantity has been experimentally investigated by Perrin for certain suspensions.

† 'Phil. Mag.,' 1892, [5], vol. 33, p. 468.

‡ 'Phil. Trans.,' 1886, vol. 177, p. 679.

§ 'Phil. Mag.,' 1899, [5], vol. 47, p. 501.

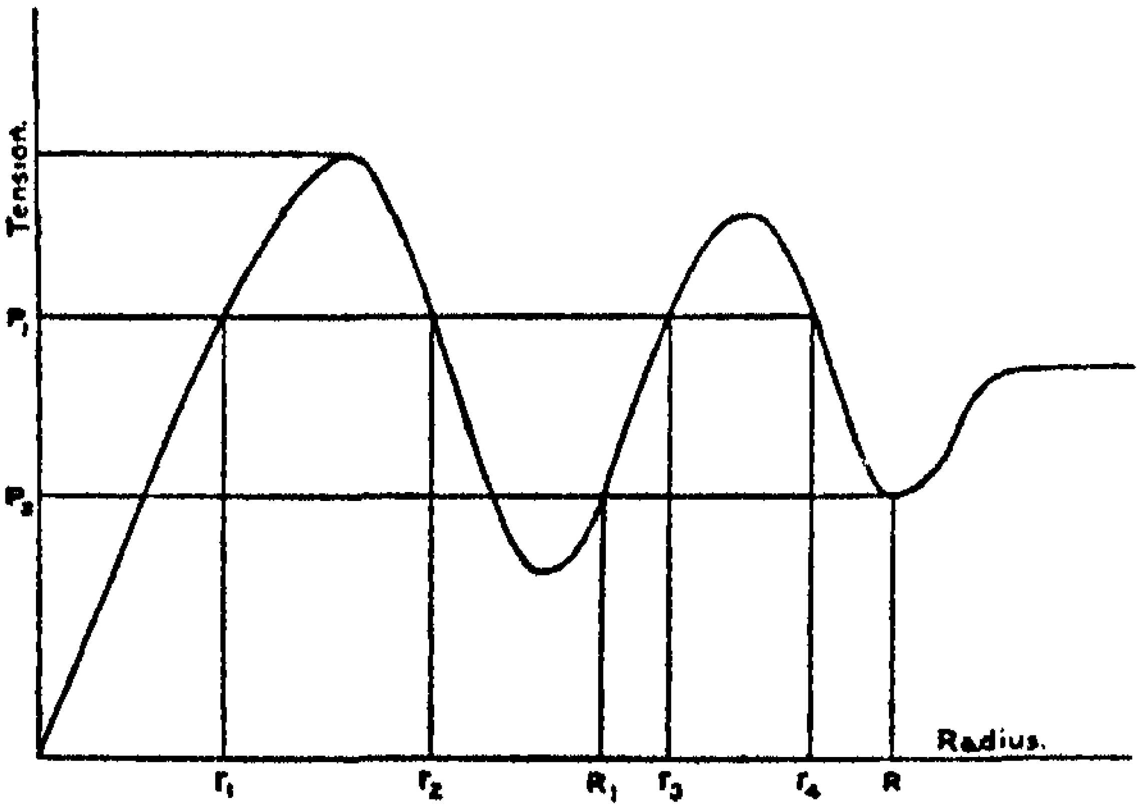

Fig. 1.

At pressure P′, globules of radius r_1, r_2, r_3, r_4 can co-exist, but those of radius r_2 and r_4 will probably be unstable.

According to the accepted theory, the tension of a film is constant so long as the thickness is greater than twice the range of molecular action. That portion of the curve in the figure which lies between $r = 0$ and R relates to a system whose globules are so small that the radius is less than the range of molecular attraction. It follows, therefore, that so long as the globule substance has not the properties of a phase in mass, *i.e.* so long as $dt/dr>0$, a state in which the interior mass is present as globules is stable, and the globules may be of different radii, also the osmotic pressure of the solution will not be fixed by fixing the ratio of the masses of the components and the temperature. These are the characteristics of a colloidal solution, and it is therefore obvious that a determination of the form of the function dt/dr is of fundamental importance in the theory of such solutions.

The evidence that in certain films tension varies discontinuously with thickness is complete. Reinold and Rücker determined the thickness of the black area in a soap film to be about 12 $\mu\mu$, and found that at the edge of the area the film thickened abruptly to 50 $\mu\mu$ or more. Since the tension of a horizontal film must be everywhere the same, the tension of the film 12 $\mu\mu$ thick is also that of the thicker film. The abruptness of the transition between thin and thick regions can only mean that films of intermediate thickness are unstable,* and that between certain thicknesses tension increases as thickness diminishes. Johannot's experiments make it probable that when the tension of the film is considered as a function of the thickness there is more than one maximum.

It is commonly held by physicists that these results obtained by the study of films of fluid immersed in air can be applied to variations of the tension of a globule of fluid immersed in its own vapour.† The likelihood of this being true depends upon the view that is taken of the significance of these maxima and minima.

If they are due to something fundamental and fixed in the nature of the field of force about an atom or a molecule, they will appear in all expressions for the energy of a mass or layer of matter whose dimensions are less than the range of the force.

Maxwell‡ showed that if the mutual attraction between the molecules of a fluid changes to a repulsion when the distance separating the molecules is less than a certain quantity, the tension of a film would begin to increase with decreasing thickness when the thickness was equal to this quantity, and Reinold and Rücker§ suggest that the increase of tension which they found in the films $50\,\mu\mu$ thick is due to this cause. J. J. Thomson‖ finds in the corpuscle theory of atomic structures justification for the view that the extra atomic field of force has zones of attraction and repulsion. It is obvious on this theory that the field must be complex, for consider the simplest model of an atom—a central core of stationary electrons surrounded by a plane ring of rotating electrons. There will be a field due to the stationary electrons in which the electric intensity will vary inversely with the square of the distance from the centre of the atom. And there will also be an electromagnetic field due to the rotating ring in which the intensity varies along that radius which is at right angles to the plane of the ring inversely with the cube of the radius.

On purely theoretical grounds, therefore, Boscovich's conception of a field of force about an atom whose sign changes as the distance from the centre of the field increases has some justification, and, as is well known, Kelvin¶ applied this conception to capillary phenomena. The assumption that maxima and minima occur in the variation of the tension with the radius of a drop of fluid also offers a singularly simple and direct explanation of the influence of electrically charged nuclei upon the condensation of supersaturated vapour,* and, as we have seen, it would furnish an equally direct interpretation of the peculiarities of many colloidal systems.

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* Reinold and Rücker, *loc. cit.*

† Thomson, 'Conduction of Electricity through Gases,' 2nd Edition, p. 163; Thomson and Poynting, 'Properties of Matter,' p. 168.

‡ 'Encyc. Brit.,' art. "Capillarity."

§ *Loc. cit.*, p. 681.

‖ 'The Corpuscular Theory of Matter,' London, 1907, p. 158.

¶ 'Mathematical and Physical Papers,' vol. 3, pp. 398 and 409

Unfortunately much may be urged against the view that these maxima and minima in the tension of a soap film have any direct relation to the field about an atom or molecule.

It must be borne in mind at the outset that a drop of water immersed in its own vapour is a system composed of one component, and that variations in the tension of the drop with the radius can, therefore, be due only to the nature of the field of force between the molecules of water. That is to say, it depends solely upon the form of the function $\phi(f)$ in the Young-Laplace theory of capillarity. But the soap films with which Reinold and Rücker and Johannot worked contained two components at least, and were composed of colloidal solution, that is, of a peculiarly complex type of fluid. If maxima and minima did exist in the tension of a drop of pure water of radius less than the range of the mutual attraction of the molecules, it should be possible to form films of pure water just as it is possible to form films of soap solution. This is not so. A film of water breaks with very great rapidity; in fact, it behaves as it should if tension decreased very rapidly with the thickness of the film.

The repulsion suggested by Maxwell, and needed to account for the peculiarities of soap films, can perhaps be found in quite another direction. In a previous paper I described the existence of a remarkable potential difference between a film of impurity,† such as an oil, floating on the surface of water and the subjacent water. It occurred to me, when conducting the experiments, that if such a surface were lifted up to form a free film, as it can be lifted up by slowly withdrawing a solid frame from the fluid, it would consist of three layers, two outer ones at a potential higher or lower, as the case may be, than the interior layer. The arrangement would be such as is shown in the diagram (fig. 2).

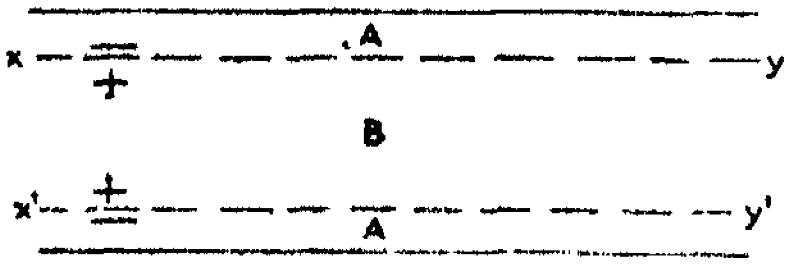

Fig. 2.

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* J. J. Thomson, 'Conduction of Electricity through Gases,' *loc. cit.*

† 'Roy. Soc. Proc.,' 1911, B, vol. 84, p. 220; compare also Reinold and Rücker, 'Phil. Trans.,' 1893, A, vol. 184, p. 527.

A, A, are films of oil which may be from 0·5 to 10 $\mu\mu$ thick, and at the interfaces $x'y'$, xy, a constant difference of potential is found due to polarisation of the matter on either side.

Let the fluid B drain away. The positively charged portion of the fluid on either side is of finite thickness, owing to molecular movements. When B has drained away so that the extreme oscillations of the positively charged molecules at x are brought into the electric field about the positive molecules at x', there will be a repulsion. If the film thin further it must first entirely reconstruct itself. The first state may be that of soap film showing Newtonian colours; the second, that is after reconstruction, may be that of a black film.

This theory finds justification in a study of the actual films. The experiments and apparatus will be described more fully in a later paper. For the present it will be sufficient to refer briefly to two typical cases.

A film, 1 × 2 cm., of soap, starch, or saponin solution in water, with air on each side, was so arranged that it could be inspected under the microscope while a constant current was passed through it. Lycopodium dust, or specially prepared French chalk, was dusted on to the film, and also immersed in it, and it was noticed that the unimmersed particles moved in the electric field in a direction opposite to that of the immersed particles.

Measuring movement in the divisions of a micrometer eyepiece covered in five minutes, I found :—

	Direction. + −	Distance.	
Saponin-water film—			
Unwetted particles on the surface	—	0	
Middle of the film	⟶	12	
Starch-water film—			
Unwetted on surface	⟶	10 }	15 }
Immersed	⟵	10 }	7 }

That is to say, it was possible to observe particles at different levels in the film moving in opposite directions at the same time, the direction of the movement of each particle being reversed on reversing the direction of the electric current. These observations can, I think, mean only one thing, namely, that such films are composed of layers between which there is a contact difference of potential.

Let us agree to call the various surfaces of such composite films interior and exterior surfaces. There will then be in the case of a film of fluid in air two exterior and two interior surfaces, and in the case of a film of one fluid on the surface of a mass of another fluid two surfaces, one interior and one exterior. In the same way there will be in the former case one interior and two exterior layers, and in the latter an exterior layer and an interior mass.

When all the layers have a thickness exceeding twice the range of action of any molecules present in the layers, the sum of the tension of the layers and the electric density at the interfaces will be constant and independent of a variation in thickness of any or all the layers. When the thickness of all or of any one layer is less than this magnitude the tension and the electric density vary, and may be considered functions of the thickness. It is of importance, therefore, first of all to determine whether the range of molecular action is a fixed value or whether it is dependent upon the chemical nature of the molecules concerned. The question is considered in the next paper.

The Tension of Composite Fluid Surfaces and the Mechanical Stability of Films of Fluid.

By W. B. Hardy, F.R.S.

(Received March 13,—Read May 16, 1912.)

The tension of a composite surface composed of a fully separated layer of one fluid (say oil) spread over a mass of another fluid (say water) is given by the equation

$$T = T_A + T_{AB}, \tag{1}$$

where A and B denote respectively the oil layer (exterior layer) and the water (interior mass).

If z be the depth of the exterior layer, then, for a given temperature θ, the quantity T_A will reach a constant value when z is either $>$ twice the range of action of the oil molecules on each other, or $>$ the sum of two values, namely, the range of action of oil molecules on each other, and of the oil molecules on the water molecules. Let Z be the lowest value of z for which T_θ is constant: $\frac{1}{2}Z$ is equal to the greater of two quantities, the range of action of the molecules of oil, or the mean of this value plus the range of action of these molecules upon the molecules of water.

The attractive force between two molecules in the theory of capillarity is a force which decreases rapidly as the distance between the molecules increases. Young assumed the force to be negative, that is to say, a repulsion, over a very small distance, positive beyond this distance, and constant until it vanished at a distance large in relation to the depth of the zone of repulsion, but very small relatively to distances directly appreciable by our senses. Maxwell assumed the force to vary inversely with the fifth power of the distance. Whatever the form of the function may be, that which is measured when tension is taken as an index of the range is not necessarily the absolute limit of the field of force about a molecule, but the limit of its sensible action.

It can be proved that

$$T_{AB} = T_A + T_B - 2T'_{AB}, \tag{2}$$

the term $2T'_{AB}$ being the work gained per unit area when a surface of A is allowed to approach normally a surface of B.* The full expression for the tension T of a double surface is therefore

$$T = 2T_A + T_B - 2T'_{AB}. \tag{3}$$

This expression, and the equation $T = T_B$, are the values of T for the limits $z = Z$ and $z = 0$ respectively, and it should be possible to pass from one to the other without a break by gradual increments of the fluid A. For all thicknesses of $A > Z$, T is constant, therefore it would appear that Z could be determined by measuring the minimal thickness of A for which T is constant.

Obviously A must be a pure substance, for if it contained an impurity whose molecular relations to B were such that it reduced the tension of B more effectively than pure A, the tension T_{AB} would be constant and minimal only when the mass of the external layer (A*a*) per unit area was great enough to saturate the interface with *a*.

The conditions which determine the spreading of one fluid over another, or rather between two others, one of which is air, may be stated as follows:— Denoting the third fluid, air, by C, then at the edge of a flat drop of A three forces have to be resolved due to the three tensions. "If the three fluids can remain in contact with one another, the sum of any two of the [tensions] must exceed the third, and by Neumann's rule the directions of the interfaces at the common edge must be parallel to the sides of a triangle, taken proportional to T_{AB}, T_{BC}, T_{CA}. If the above-mentioned condition be not satisfied, the triangle is imaginary, and the three fluids cannot rest in contact, the two weaker tensions, even if acting in full concert, being incapable of balancing the strongest. For instance, if $T_{CB} > T_{AB} + T_{AC}$, the second fluid spreads itself indefinitely upon the interface of the first and third fluids." . . . . "The experimenters who have dealt with this question—Marangoni, van der Mensbrugghe, Quincke—have all arrived at results inconsistent with the reality of Neumann's triangle. Three pure bodies (of which one may be air) cannot accordingly remain in contact. If a drop of oil stands in lenticular form upon a surface of water, it is because the water-surface is already contaminated with a greasy film."* Further, the Young-Laplace theory of capillarity leads, according to Lord Rayleigh, "to the important conclusion, so far as I am aware hitherto unnoticed, that, according to this hypothesis, Neumann's triangle is necessarily imaginary that one of three fluids will always spread upon the interface of the other two." The preceding pages present what I believe to be the current theory of the tension of composite surfaces; my own experiments prove that it is too narrow for the facts.

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* See the preceding paper, p. 604; also Lord Rayleigh, 'Phil. Mag.,' 1890, [5], vol. 30, p. 460.

When some ricinolic acid (Kahlbaum) is placed upon a clean surface of water the quantity first added spreads with great rapidity, but when the film is somewhere about $40\mu\mu$ thick, any further quantity added refuses to spread, but remains permanently gathered into a lens. When more acid is added to the lens it enlarges until the whole surface is covered with a layer of the oil which has been forced over it by gravity. Clearly, therefore, whereas the first added oil spreads because it lowers the tension, the sign of the effect changes at a certain stage in the thickening of the layer A, further thickening increasing the tension. The spreading of the oil is therefore resisted, and a lens is formed. With some substances (olive oil, cymene, heavy oil), before the stage is reached at which a drop refuses to spread, small lenses, just visible to the naked eye, appear dotted all over the surface. In the case of cymene these tiny lenses are just visible when the film A is of an average thickness of $100\mu\mu$, calculated on the assumption that its density is that of cymene in mass. The phenomena can be followed in detail by adding successive drops of "heavy oil"† at the same spot. The result is a patch which is bounded by rings. Each drop allows the one last added to contract to a ring. The rings are of the same breadth when the drops are of equal size. The outermost ring of all—very visible when heavy oil is used—is the contracted field of contamination on the surface before the oil is added. The colour of the rings slowly changes. A drop of heavy oil spreads first to a patch of superb blue, then changes to purple with a defined yellow edge, 1 mm. wide, the patch being (say) 5 cm. across. The patch, up to now uniform, begins to become mottled, the red gives way to a beautiful pattern of peacock green, steel blue, and bronze yellow, the various colours being sharply marked off from one another even under considerable magnification. In the centre of each blue patch, which in an undisturbed surface is accurately circular, is a small lens of oil, appearing as a point only to the naked eye.

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* Lord Rayleigh, *loc. cit.*, p. 463.

† Distilled from Price's "Motorine A," see later.

The mode of formation of these lenses is clear. Each is a droplet of oil condensed about some nucleus, for the most part solid, much more rarely a tiny bubble of gas. They appear on a surface of distilled water greased with the heavy oil when the average thickness of the film is approximately 200 $\mu\mu$. The surface except at first is therefore highly complex—coloured areas and lenses being in tensile equilibrium.

In these cases when the general surface is nearly saturated with oil, that is, when the minimum of surface energy is nearly reached, condensation occurs on any nuclei which may be present. The ultimate relation is the same as that found for ricinolic acid, or, indeed, for all the substances experimented with (olive oil, castor oil, croton oil, ricinoleic acid, benzyl cyanide, "heavy" oil, cymene and benzene): a uniform sheet of a third fluid in mass* can only be inserted between the fluids air and water by the operation of an external force, namely gravity.

It is obvious from equation (1) that T must have a minimal value unless the rate of decrease of T_{AB} is equal to the rate of increase of T_A. For, let it be supposed that oil could be spread evenly and continuously on water until it reached the thickness Z at which it forms a separate phase, the first oil spread on the surface causes the tension T_B to fall, but the last of the oil added is causing tension T_A to rise, and the rise may more than compensate for any further fall in T_B. An approximate equation for the surface may be got as follows. Consider a large lens of oil, say 10 cm. in diameter and about a millimetre in thickness. Such a lens can readily be formed. Its surface is sensibly flat, but at the edges it curves down to meet the general surface of the fluid, which is also depressed at the edge. Let the tensions of the flat surfaces be denoted by T_1, T_2, T_3. Then

$$T_1 = T_A + T_C - 2T'_{AC}, \qquad T_2 = T_A + T_B - 2T'_{AB}. \tag{4}$$

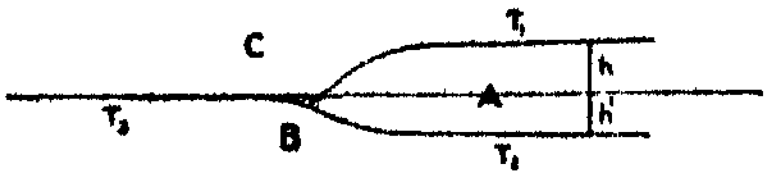

FIG. 1.

Let *a* be the area of a horizontal section of the lens, *h* the height of the upper surface above the mean level of the fluid, *h'* the depth of the lower plane surface below the mean level, and ρ the density of A, ρ' of B. Then for the potential energy of the drop we have, if the effects of curvature at the edge be neglected,

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* That is a sheet whose depth is > Z, so that the substance is present as a fully separated phase.

$$\psi = [\mathrm{T}_1 + \mathrm{T}_2 - \mathrm{T}_3 - \tfrac{1}{2} g (\rho h^2 - \rho h'^2 + \rho' h'^2)]\, a. \tag{5}$$

All the terms in this equation are constant, except h, h', and a, which are related variables.* We may therefore put

$$\frac{d\Psi}{da} = 0, \tag{6}$$

and

$$\frac{d\Psi}{da} = \mathrm{T}_1 + \mathrm{T}_2 - \mathrm{T}_3 - \tfrac{1}{2} g (\rho h^2 - \rho h'^2 + \rho' h'^2) - g \left(\rho h' \frac{dh}{da} - \rho h' \frac{dh'}{da} + \rho' h' \frac{dh'}{da} \right). \tag{7}$$

dh'/da and dh/da are very small quantities, so that the whole of the last term may be neglected.

From (4), (6), and (7) we get

$$\mathrm{T}_3 = \mathrm{T}_\mathrm{A} + \mathrm{T}_\mathrm{C} - 2\mathrm{T}'_\mathrm{AC} + \mathrm{T}_\mathrm{A} + \mathrm{T}_\mathrm{B} + 2\mathrm{T}'_\mathrm{AB} - \mathrm{K}g,$$

in which the term depending upon gravity is written $\mathrm{K}g$ for brevity. The tension of the gas T_C may certainly be neglected, and probably T'_AC, which represents the energy per unit area of the gas or vapour condensed on to the surface of the lens.

There remains

$$\mathrm{T}_3 = \mathrm{T}_\mathrm{A} + (\mathrm{T}_\mathrm{A} + \mathrm{T}_\mathrm{B} - 2\mathrm{T}'_\mathrm{AB}) - \mathrm{K}g, \tag{8}$$

and the term in brackets is equal to T_AB.

If T_3 were equal to T_AB then $\mathrm{T}_\mathrm{A} = \mathrm{K}g$, that is to say the lens is maintained against the action of gravity solely by the tension of its air surface, that is by the tension of the oil itself.

But there is no necessary equality between T_3 and T_AB. They refer to essentially different things. T_3 is the potential per unit area of a "film of discontinuity," to use Gibbs' phrase, between water and air whose tension is reduced by a concentration Γ per unit area of a component A. T_AB on the other hand refers to a surface of discontinuity between A and B both in mass.

In the application of capillary theory to the solution of the equilibrium of three fluids it is usual to consider the tensions as forces which meet at a point. The theorem known as Neumann's triangle may be quoted as an instance. The method seems to me open to grave objections. It is true, as Gibbs has shown, that the energy of a surface layer may be equated to a strain limited to a mathematical surface, the "surface of tension," and, therefore, at the meeting place of three fluids these surfaces will intersect in a line, but since the range of action of molecular forces is finite the tensions of the surfaces cannot be the same for a finite distance from the line of intersection, the distance being the greatest distance at which any of the molecules present act upon one another. The alternative assumption is absurd, namely, that there is no mutual attraction between the material composing the three films right up to the mathematical intersection of the "surfaces of tension."

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* ρ appears only in the term relating to gravity, and may be taken as constant over that range in which this term has a sensible value.

At the edge of the lens there is equilibrium, so that

$$t_3 = t_1 \cos\theta_1 + t_2 \cos\theta_2; \tag{9}$$

but t_1, t_2, and t_3 must not be identified with T_1, T_2, and T_3.

All interfaces which I happen to have observed have been highly polarised, the work T'_{AB}, therefore, in those cases must include at least two terms, one for the work per unit area needed to produce electrification of density σ and $-\sigma$, and another for the work due to simple molecular attraction. If the sum of all the molecular forces which contribute to the self-attraction of the matter be included in the phrase "molecular attraction," the electric energy ceases to be a separate term. But if any attempt be made to distinguish between the kind of attractions, *e.g.* chemical or physical, two terms must be employed.

The actual phenomena are undoubtedly better represented by two terms. Consider the tension T_2, which is equal to T_{AB}. We have, as before,

$$T_{AB} = T_A + T_B - 2T'_{AB}.$$

In forming this surface, by allowing unit areas of surfaces A and B to approach normally, let the work $2T'_{AB}$ be gained in two steps, that is to say, when the surfaces come into contact, let work be first gained by the operation of the mutual attraction of unchanged molecules of A and B; call this work per unit area $2T'_{ab}$. The molecules then proceed to alter one another so that polarisation occurs and work per unit area is done equal to $f(\sigma)$. Since the necessary condition of equilibrium of a film of discontinuity is that the tension shall be "less than that of any other film which can exist between the same homogeneous masses,"* we may conclude that the effect of polarisation is to make the tension less. We have, therefore, the relation

$$2T'_{AB} = 2T'_{ab} + f(\sigma) \tag{10}$$

and

$$T_{AB} = T_A + T_B - 2T'_{ab} - f(\sigma). \tag{11}$$

Owing to molecular movements, the polarised molecules occupy layers of finite thickness, but we may with Helmholtz consider the two electricities as distributed on two parallel surfaces as in a condenser, the plates of which are separated by a very small distance x and have an area a. Polarisation will be complete, that is, the electric density will be maximal, only when the film of A shall have reached a certain thickness, which may or may not be the same as the extreme range of attraction of the molecules of A and B. In other words, σ and x and, therefore, the electric energy of the surface, are functions of the mass of A per unit area.

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* Gibbs, *loc. cit.*, p. 403.

$$f(\sigma) = 2\pi x\sigma^2$$

and, with (8) and (11) we have

$$T_3 = 2T_A + T_B - 2[T'_{ab} + \pi x\sigma^2] - Kg. \qquad (12)$$

It is important to realise distinctly the meaning of the terms T'_{ab} and $f(\sigma)$. The former is that fraction of the work gained when unit area of a surface of pure A approaches normally unit area of a surface of pure B due to the Laplacian attraction of molecules of pure A, say oil, for pure B, say water. On the corpuscular theory of matter, it is the term which expresses the work gained from the mutual influence of the external or stray fields of the molecules. The latter term, $f(\sigma)$, is that portion of the work, assumed to be expended entirely in producing polarisation, which is due to chemical action between the molecules. It is therefore the term which expresses the sum of the change in the internal fields of force of the molecules. If A does not react chemically with B at the interface, $f(\sigma) = 0$, and T'_{AB} is equal to the work gained by simple Laplacian attraction. This distinction may seem artificial, but it will be seen that it is needed in order to explain the actual phenomena. It must also be made in any complete specification of the intrinsic energy of some fluids. Consider, for instance, benzene and water. In the former, self-attraction, so far as we know, is entirely due to the stray field of the stable ring of atoms which forms the molecule. In the latter, a fraction of the total self-attraction, a very small fraction it is true, is due to dissociated molecules, that is, to the opening out of the internal molecular fields.

It must be borne in mind in considering the polarisation of an interface between such bodies as oil and water that the phenomena may be partly due to electrolytes present as "impurities." Certainly they cannot be without influence, and equally certainly they cannot be wholly excluded (*e.g.* the carbonic acid of the air). But in colloidal solutions the charge on the colloid masses is always greatest when the concentration of electrolytes is least, and I have found that a slight leakage of zinc sulphate from the non-polarised electrodes into the observation chamber completely arrests any migration at an interface. According to our present knowledge such interfaces are discharged, not charged, by soluble electrolytes, but further experiment is both needed and difficult.

Experimental Methods.—The tension was determined in two ways. In the first, usually called Wilhelmj's method, the weight needed to balance the pull exerted by the fluid on a thin blade hung vertically is measured by a balance; in the second, the weight needed to detach a flat plate from the surface is measured.

Five glass blades, each 0·15 mm. thick, were mounted in a light frame so that they were parallel to each other and 1 cm. apart. The frame and blades were suspended from one arm of a balance and the level adjusted by means of a fine screw so that the lower edge of the blades was as nearly as possible at the mean level of the fluid when the pointer of the balance stood at zero. If l be the total length of the blades, m the weight needed to balance the pull, the tension is given by $T = mg/2l$. This formula assumes that the angle of contact of fluid and glass is zero. The assumption is sensibly true for clean water and nearly true for a contaminated surface. The factor to correct for the angle is its cosine, and, as this decreases in value very slowly for small angles, the correction is small. But, though small, it must not be lost sight of. The effect of ignoring this correction is to make the calculated values of the tension too low when the water surface is much contaminated. The formula cannot be used to obtain the tension of a double surface A and AB, for the angle of contact of the AB surface with the glass seems in all cases to be considerable.

In prolonged experiments, it is very necessary to inspect the blades from time to time with a hand lens, to see that no "beading" has taken place owing to impurity condensing on to the surface of the glass from the air.

The formula usually given for the plate method also assumes the angle of contact between fluid and plate to be zero at the moment of breaking. The formula is at best an approximation, and the error may be considerable. As the best approximation, I used the following, $T = (m \times 503)^2/g\rho$, and the weight m was always taken as the mean of the weight which the surface would just hold, and the weight which broke the plate away. The plate method has this advantage, that it can be applied when only a small quantity of fluid is available. It was therefore used only to obtain an approximate value for the tension of the substances used to form the film on the water.

The thickness of the film was varied either by Miss Pockel's method,* in which the mass of the film is constant and the area varied, or by gradually thickening a film by increments of material, the surface being constant.

The ordinates of the curves in all cases are tension in dynes per centimetre, the abscissæ are the thickness of the film calculated from the weight of material placed on the surface, and the area of the surface, the density of the film being taken as that of the substance in mass. I did not succeed in weighing the minute quantities of croton oil used, and the abscissæ for this curve are therefore on an arbitrary scale, the unit 1 being probably much less than 1 $\mu\mu$.

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* 'Nature,' 1891, vol. 43, p. 437; also Lord Rayleigh, 'Phil. Mag.,' 1899, [5], vol. 48, p. 331.

Except when the contrary is stated, freshly distilled water from a silver still was used. The trough, which was of tin plate, measured 71 × 10 × 1 cm. The most satisfactory barriers were made of tin plate 1·5 cm. wide, with a vertical strip of plate slightly less than 10 cm. long, and about 0·75 cm. deep, soldered (with tin) to the middle. Each blade in transverse section was thus T-shaped. Two blades were always used, and kept about half a centimetre apart or less, so as to obviate leakage from a contracted film. Direct leakage was, I think, practically absent—at any rate, lycopodium dusted on to the cleaned surface just near the blade failed to reveal it. But, of course, the contracted and the cleaned surfaces are in communication with the mass of the liquid, and, if the substance used to contaminate the surface is at all miscible with water, solution from the contracted surface and condensation on to the clean surface will go on. The vertical strips on the blades were placed there to "wire-draw" any diffusion stream. The influence of solubility on the equilibrium of a surface needs careful consideration; for the present, it may probably be neglected owing to the extreme insolubility in water of the substances experimented with. The water surface was cleaned by sweeping any contamination to one end with one of the blades It was then got rid of by a quick jerk, which threw the surface out of the trough. Lord Rayleigh* has measured the tension of clean and contaminated surfaces of water by the ripple method and by the blade method. The values obtained are more divergent the greater the degree of contamination:—

	Blade method.	Ripple method.	Difference.
Clean water	74	74	0
Camphor point	57·7	53	4·7
Saturated with olive oil	[About 48]*	41	7

* Measured by myself.

Owing, however, to the hysteresis of the surface, the ripple method itself cannot be relied upon to give correct results.

The sources of error in the blade method are of contrary sign, and should, therefore, to a certain extent neutralise one another. As contamination increases three changes have to be considered, (1) an increase in the angle of contact of the surface with the blades, (2) a thickening of the edge of the film of fluid on the blades, which may result in "beading," and (3) any change in the tension of the fluid where it wets the blades owing to an attraction of the solid for the oil. (1) would give the relation $T_{\text{calc.}} < T_{\text{real}}$, from (2) $T_{\text{calc.}} > T_{\text{real}}$, and from (3) $T_{\text{calc.}} > T_{\text{real}}$. So long as there is no sign of beading or irregularity when the blades are inspected by a good lens, and the angle of contact appears to be nearly zero, $T_{\text{calc.}}$ is probably not far removed from T_{real}. In order to centre attention on the main point, namely, the relation of tension to chemical constitution, the hysteresis of composite surfaces is accepted throughout this paper without criticism. There is no doubt in my mind that it is a real phenomenon of the surface and not merely an effect of adjustments at the blades, since it appears when the layer of contamination is excessively thin: also Reinold and Rücker found the properties of a film to depend upon its age.

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* 'Phil. Mag.,' 1890, [5], vol. 30, p. 398.

It will be well here briefly to recapitulate Lord Rayleigh's results. The theory of the movements of camphor on the surface of water, due to van der Mensbrugghe, implies that they will take place so long as the tension of the surface is greater than that of a saturated solution of camphor. At a certain tension, therefore, which Lord Rayleigh found by the blade method to be 0·78 that of a pure water surface, the camphor movements cease.* To this particular tension he gives the name "camphor point." On the assumption that the density of a film of olive oil is the same as that of the oil in mass Lord Rayleigh found the thickness of the film at the camphor point to be 2 $\mu\mu$.† Using castor oil, not olive oil, to form the film, Lord Rayleigh measured the tension when the thickness of the film was varied by Miss Pockel's method. His curves show that up to a thickness of about 1 $\mu\mu$ the oil scarcely alters the tension, then a rapid fall sets in until the film becomes about 2 $\mu\mu$ thick. Further addition of oil has only a slight effect on the tension. The most important and the most quoted conclusion which Lord Rayleigh draws from these curves is that "if we begin by supposing the number of molecules of oil upon a water surface to be small enough not only will every molecule be able to approach the water as closely as it desires, but any repulsion between molecules will have exhausted itself. Under these conditions there is nothing to oppose the contraction of the surface—the tension is that of pure water."

"The next question for consideration is—at what point will an opposition to contraction* arise? The answer must depend upon the forces supposed to operate between the molecules of oil. If they behave like the smooth rigid spheres of gaseous theory, no forces will be called into play until they are closely locked. According to this view the tension would remain constant up to the point where a double layer commences to form. It would then suddenly change, to remain constant at the new value until a second layer is complete. . . . If we accept this view as substantially true, we conclude that the first drop in tension corresponds to a complete layer one molecule thick, and that the diameter of a molecule of oil is about 1 $\mu\mu$."†

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* 'Phil. Mag.,' 1899, [5], vol. 48, p. 334.

† 'Roy. Soc. Proc.,' 1890, vol. 47, p. 365.

The first comment to be made on these conclusions is that the oils with which Lord Rayleigh experimented are quite exceptional in their power of reducing the tension of water, and a similar train of reasoning applied to other substances seems to lead to impossible conclusions. The molecules of heavy oil and of cymene would have a diameter of 20 to 40 $\mu\mu$. Or, taking the camphor points given in the following table as the measure of a layer two molecules thick, we should have to accord diameters of from 200 to 500 $\mu\mu$ to their molecules.

Substance.	Tension (approximate).	Density.	Viscosity.	Average thickness of film on water at camphor point in $\mu\mu$.
Castor oil ...	28·6 at 22°	0·9351	Thick oil	1·59
Croton oil ...	27·8	0·9047	"	< 1·59
Olive oil ...	—	—	—	2
Cymene......	22·7	0·8700	Labile spirit	300 to 600
Heavy oil ...	26·4	0·9086	Will only just flow	300 to 1000
Benzene ...	28·36 at 15°	0·86	Light spirit	Cannot stop the movements of camphor.

Benzene spreads on a clean water surface, but a flat lens 1/10 mm. in average thickness has no observable effect upon the movements of camphor. To give this result, however, the benzene must be carefully purified by distillation and crystallisation. Impure benzene behaves very differently.

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* In one sense of the word contraction it may be said that the clean surface of water does not contract at all. When the blades are moved so as to diminish the area of a surface, motes floating on it do not move at all. This is the best test I know of the cleanliness of a surface. There is therefore no tangential contraction of the surface such as occurs and is readily seen when any "skin" of impurity is present. The diminution of area is effected solely by movement of the surface layer normal to itself. So long as this kind of adjustment can take place and only so long is there no hysteresis. All the elements of the surface (*cf.* Gibbs, p. 466) are in complete equilibrium with one another throughout any changes of area.

† 'Phil. Mag.,' 1899, [5], vol. 48, p. 335.

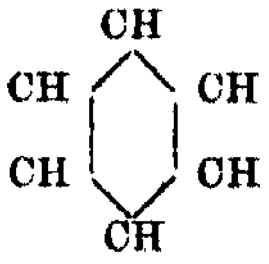
Camphor is quite "dead" upon pure benzene in mass, but still active upon a water surface carefully saturated with this substance. A surface of Cambridge tap water is very slightly contaminated. The surface must be contracted to one-tenth its area in order to produce a readable difference of tension. On such a surface of 700 sq. cm. area, 4 c.c. of benzene poured on to it forms lenses 3 to 4 cm. in diameter. These lenses show regular expansions and contractions, and smaller lenses, that is those of less diameter, move across the surface and fuse with larger ones. The expansions and contractions of the lenses are due to the tension alternately falling below and rising above that of the plane surface in the process of adjustment of the tension by horizontal spreading of a sheet of benzene from a lens and its removal by evaporation. The explanation of the pulsations therefore is the same as that which accounts for the "tears" of wine.

A touch of ether (redistilled) caused the benzene-water film to contract, owing to its tension being greater than that of the ether-water film. This is the more remarkable when it is remembered that ether is fairly soluble in water (1 in 12), and that, therefore, a large part of the ether added must be removed from the surface to pass into solution. After the addition of ether the small lenses of benzene behave differently. They move as before towards the large lenses but union seems to be impossible. When only a short distance separates small from large the former burst, the nearest point of the large lens being at the same time deeply indented. The bursting of the small lens is, therefore, accompanied by a local and temporary lowering of tension.

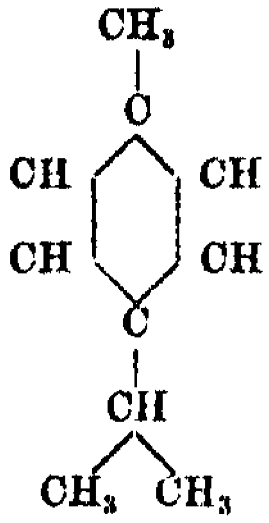
If an "active" substance be one which lowers the tension of water when a film less than $2\,\mu\mu$ thick is spread on the surface, they fall into two groups which, in order of activity, are

Active.	Relatively inactive.
Croton oil.	Benzene.
Castor oil.	Cymene.
Olive oil.	Heavy oil.

The first group contains bodies of characteristic chemical instability, namely, the esters. They are salts of unsaturated fatty acids and glycerine. Castor oil, for instance, consists mainly of the glyceride of ricinoleic acid. The "inactive" group are as characteristically stable, the heavy oil being composed of paraffin, while cymene is a benzene derivative. Benzene, the least active, has a very stable ring structure. The simple paraffins are at least as stable as benzene and the relatively large activity of the heavy oil may, therefore, be due to the presence of the "active" impurity. The "heavy oil" was obtained by distilling Price's "air cooled oil A" in a vacuum. The fraction which boils at about 400° was used and denoted by the term "heavy oil." Since the entire Price's oil A actively reduces tension this fraction may well contain a trace of active substance. In cymene the benzene ring is no longer simple, as the formula shows, and all such modifications of the benzene ring decrease its stability.



Benzene.



Cymene.

The chemical stability of benzene is associated with a remarkably slight influence on the tension of water. The molecules of the "active" substances, being organic salts, might be expected to polarise readily under an axial stress such as must be exerted at the AB surface.

Castor Oil and Croton Oil.

The curves (figs. 2, castor oil, and 3, croton oil) differ from those obtained by Lord Rayleigh in the sharp points of inflection. In order to settle whether the inflection is really as abrupt as it appears to be, the first part of the

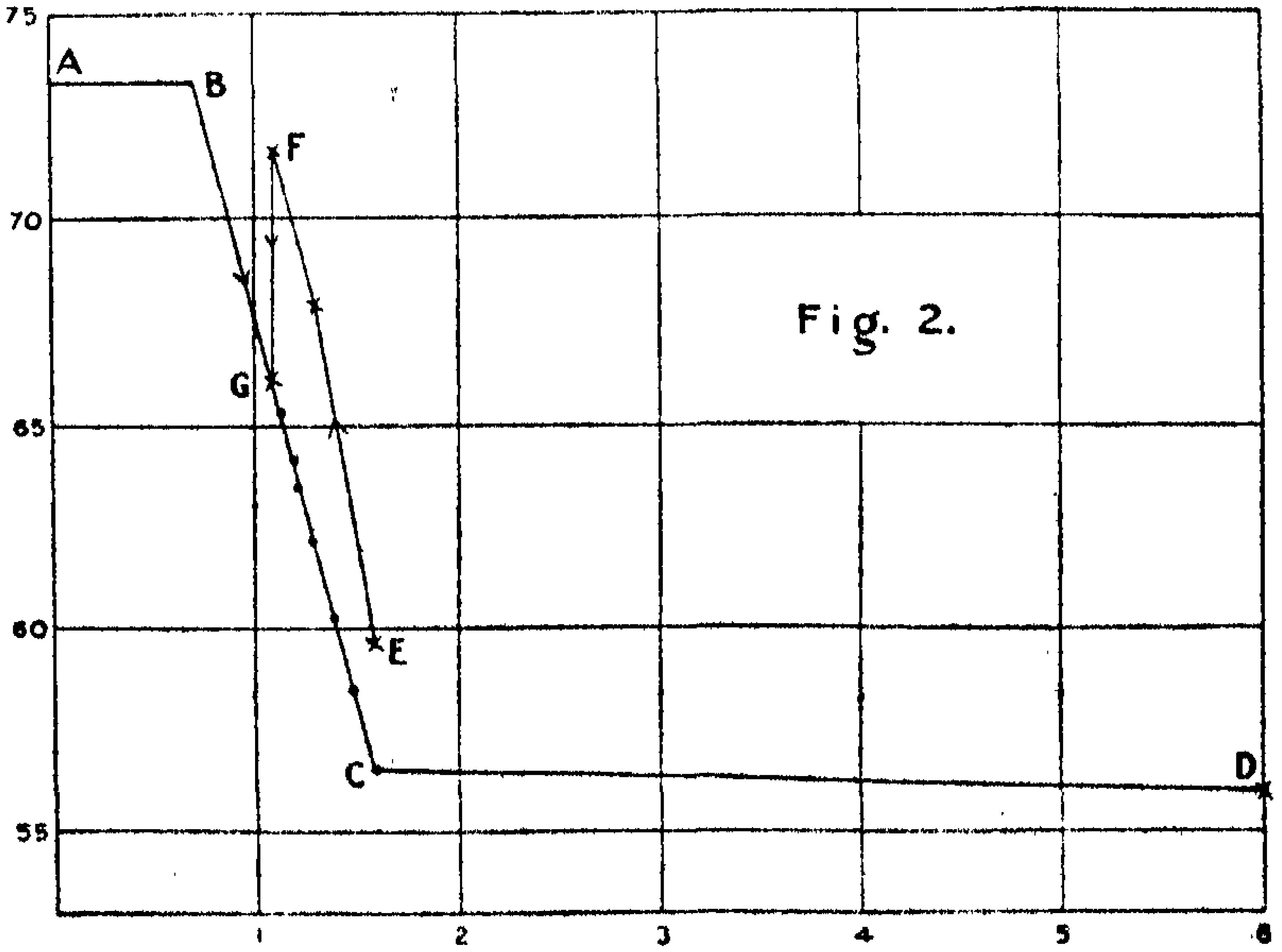


Fig. 2.

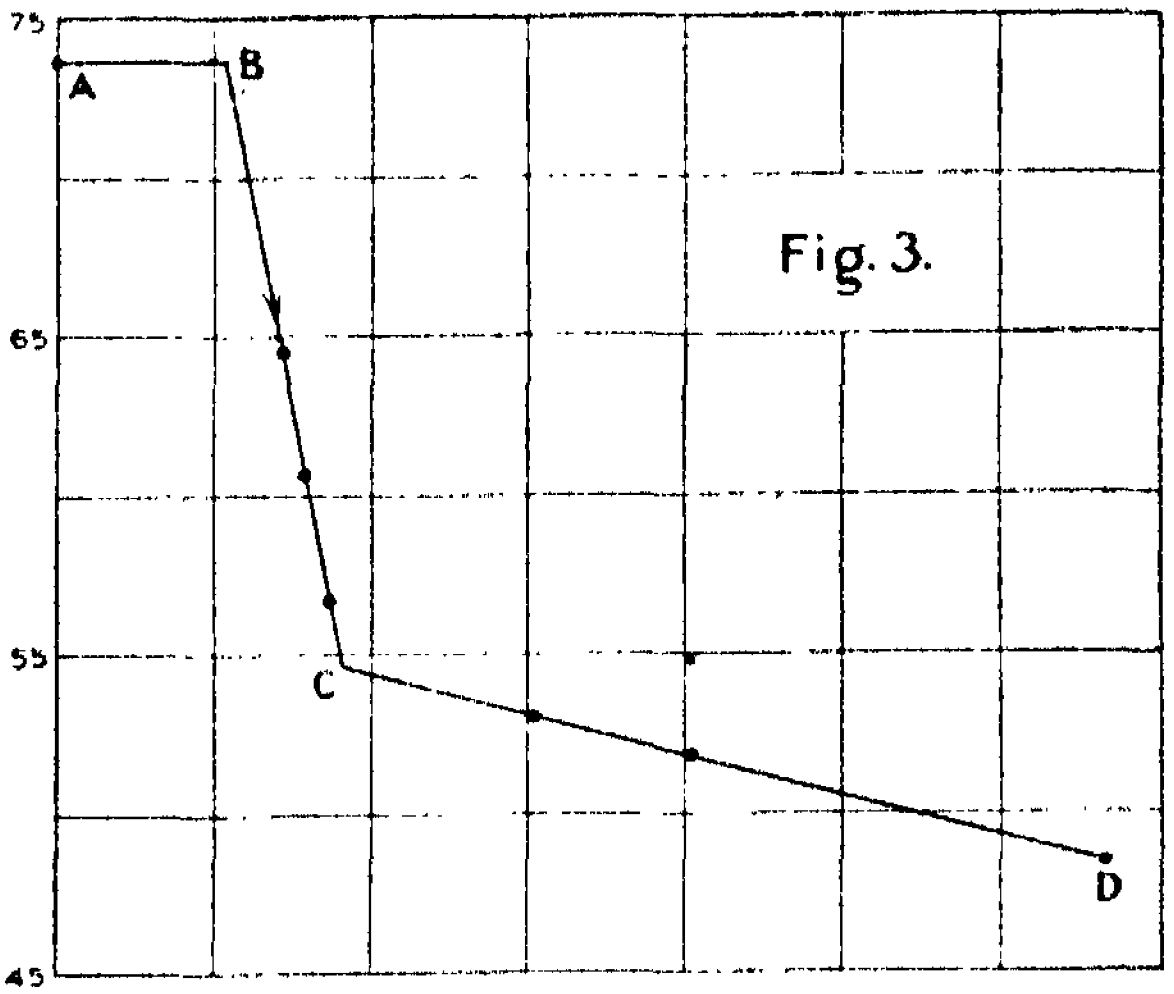


Fig. 3.

curve for croton oil was mapped with great care (fig. 4). In the figure the dots represent one series of measurements, the crosses another series, obtained

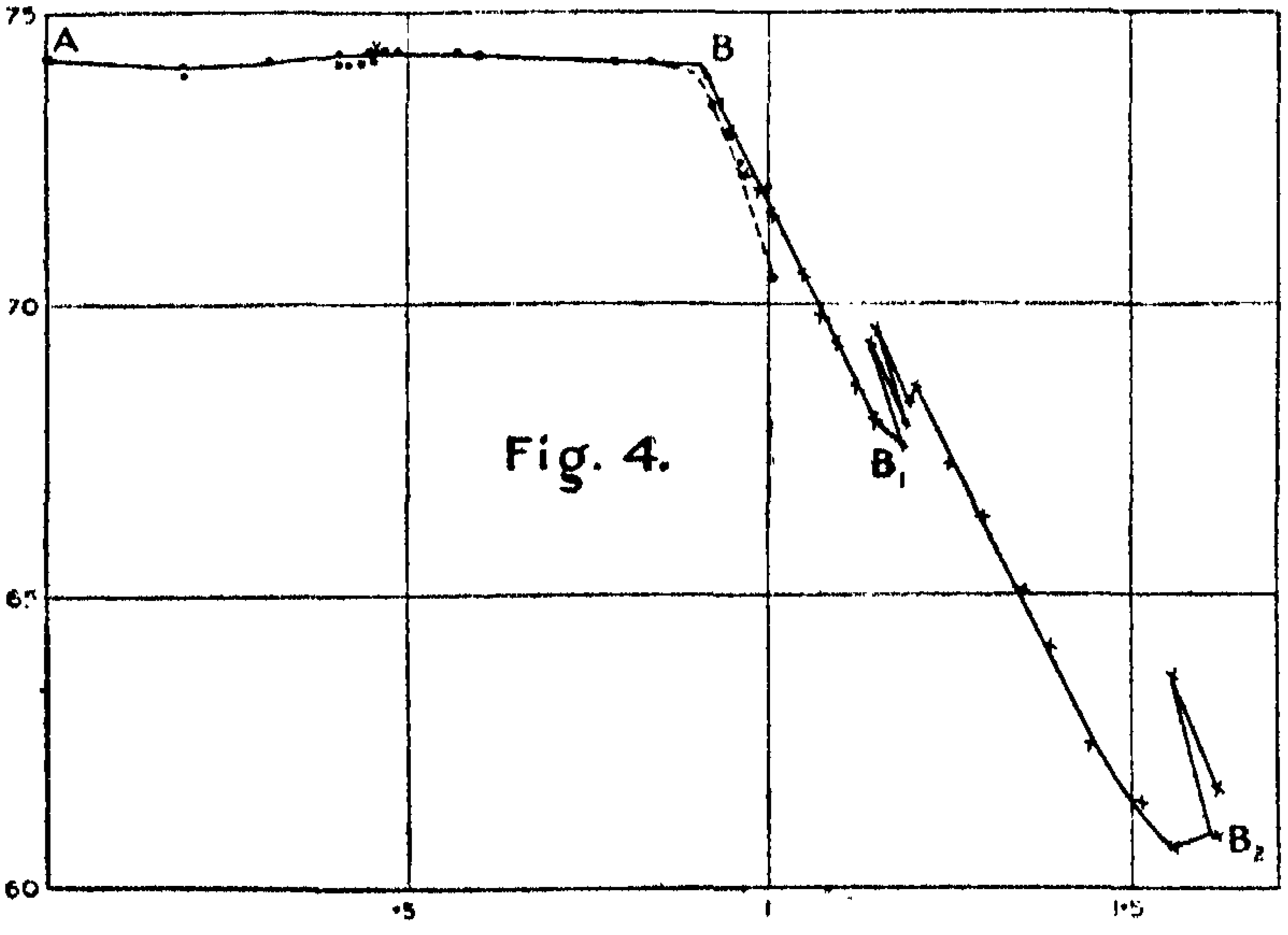


Fig. 4.

in both cases by Miss Pockel's method of varying the extent of surface. Inflection at B appears to be quite abrupt, that is to say, the crosses which lie in the first part of the descending limb lie on a straight line, which would meet the part AB at an angle. The portion AB, which is seen much magnified in curve 4, undulates, from which one may infer that the first traces of oil throw the surface into an unstable condition—obviously, it cannot be uniform, since there is not enough oil to make a layer one molecule deep, and adjustment by horizontal diffusion or spreading will be slow and difficult. In this region contraction of the surface caused a rise of tension, for instance:—

Croton Oil, a trace.

Barrier.	Tension.
68	74·1
41	74·17
31	74·27
68	74·1
31	74·17
28	74·2
22	74·2

Successive positions of the barriers are given in centimetres from that end of the trough at which the tension was being measured, and it will be noticed that, with slow contraction, the tension at 31 rose to 74·27, but, with rapid contraction, the barriers being moved quickly from 68 to 31, it rose only to 74·17.

The part BC appears to be accurately a straight line. In curve 4 it is seen to be made up of two straight lines, which are not continuous, but are joined by a cluster of points. The explanation brings out the most interesting property of these surfaces. Owing to the hysteresis, it is obvious that any accidental expansion occurring while one is mapping a curve of contraction will displace the curve—the subsequent values belong, in point of fact, to quite another curve (compare, for instance, figs. 5 and 6). The nebulæ of points therefore represent attempts which I made to return to the original curve when I had accidentally left it. The part of the curve CD slopes very slightly downward, but, as the formula for computing the tension is probably far from exact in the region CD, the particular form of the curve is here not of great importance.

Cymene.—I am indebted to my friend, Dr. Ruhemann, for a sample of this hydrocarbon. By ordinary tests it is insoluble in water. The sample was of ordinary chemical purity, probably sufficiently so to give the true value for a water-cymene-air surface. Fig. 5 needs some explanation. The curves are plotted to two distinct scales of thickness of film. The upper curves are plotted to the upper scale of 0–200 $\mu\mu$, the lower to the scale of 0–2000. Three sets of measurements are recorded: the simple dots were obtained by contracting or expanding a surface with blades, the ringed dots and crosses by adding known quantities of cymene to a surface of constant area. The agreement between the results proves that solubility of cymene in water does not produce a sensible effect, at any rate, over the first part of the curve, for the trough used contained 1½ litres of water, while for the measurements with constant area of surface only 70 cm. of water was used. The slight divergence in the later parts of the curves may be due to the difference in the mass of water employed or to the different type of surface produced by moving a barrier so as to contract the area to what is formed when successive additions of cymene are made to a surface of constant area. It has been pointed out already that a surface in contracting follows a curve different to that of an extending surface—the figure of hysteresis for cymene illustrates the point. Now, in Miss Pockel's method, a surface starts from an arbitrary point, and thenceforward is a pure contraction surface. But, when a second drop of cymene or any other substance is added, it is rapidly extended by the already existing surface, and then, after a few oscillations, comes to rest. The surface, as formed, is thenceforward composite, being partly a surface of expansion, partly a surface of contraction.

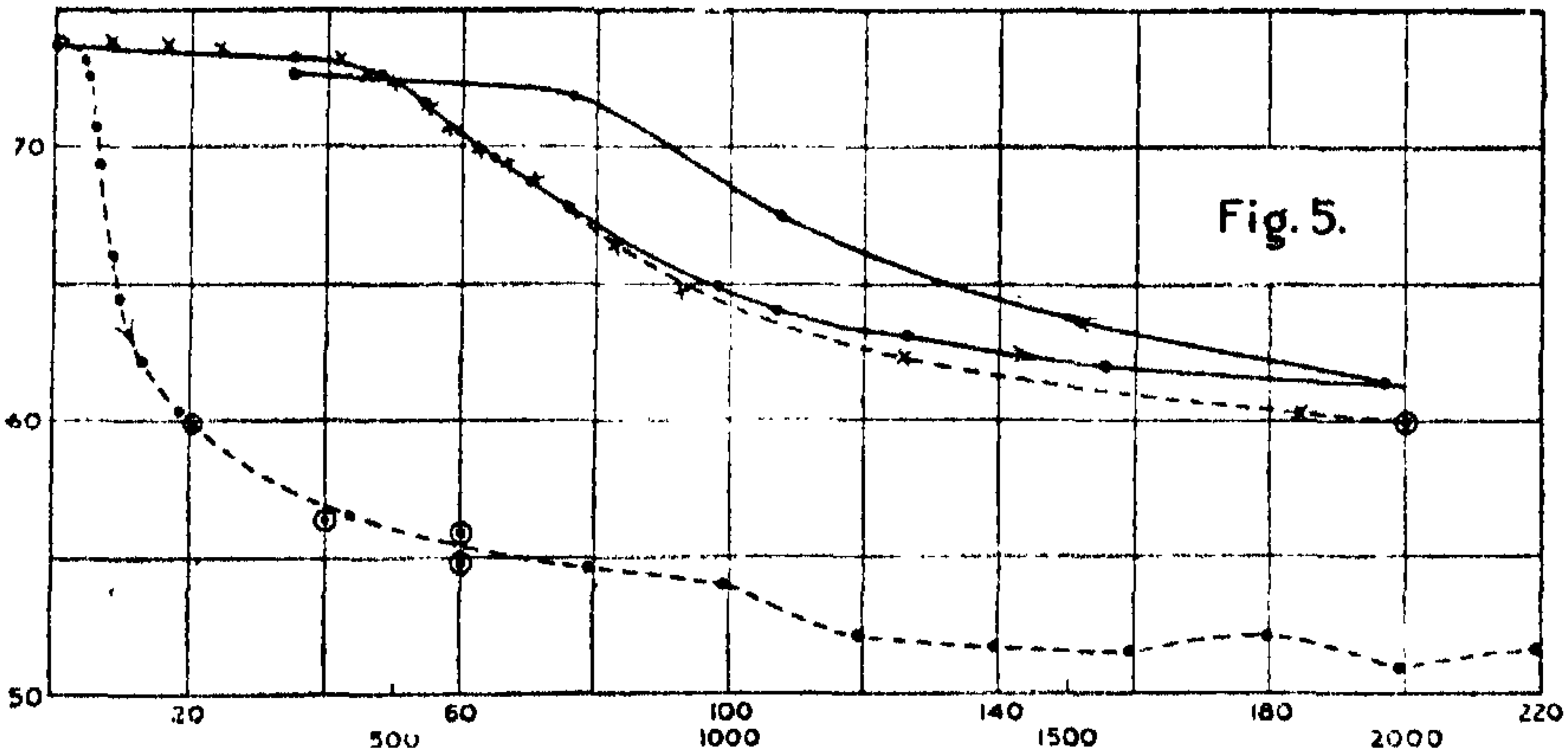
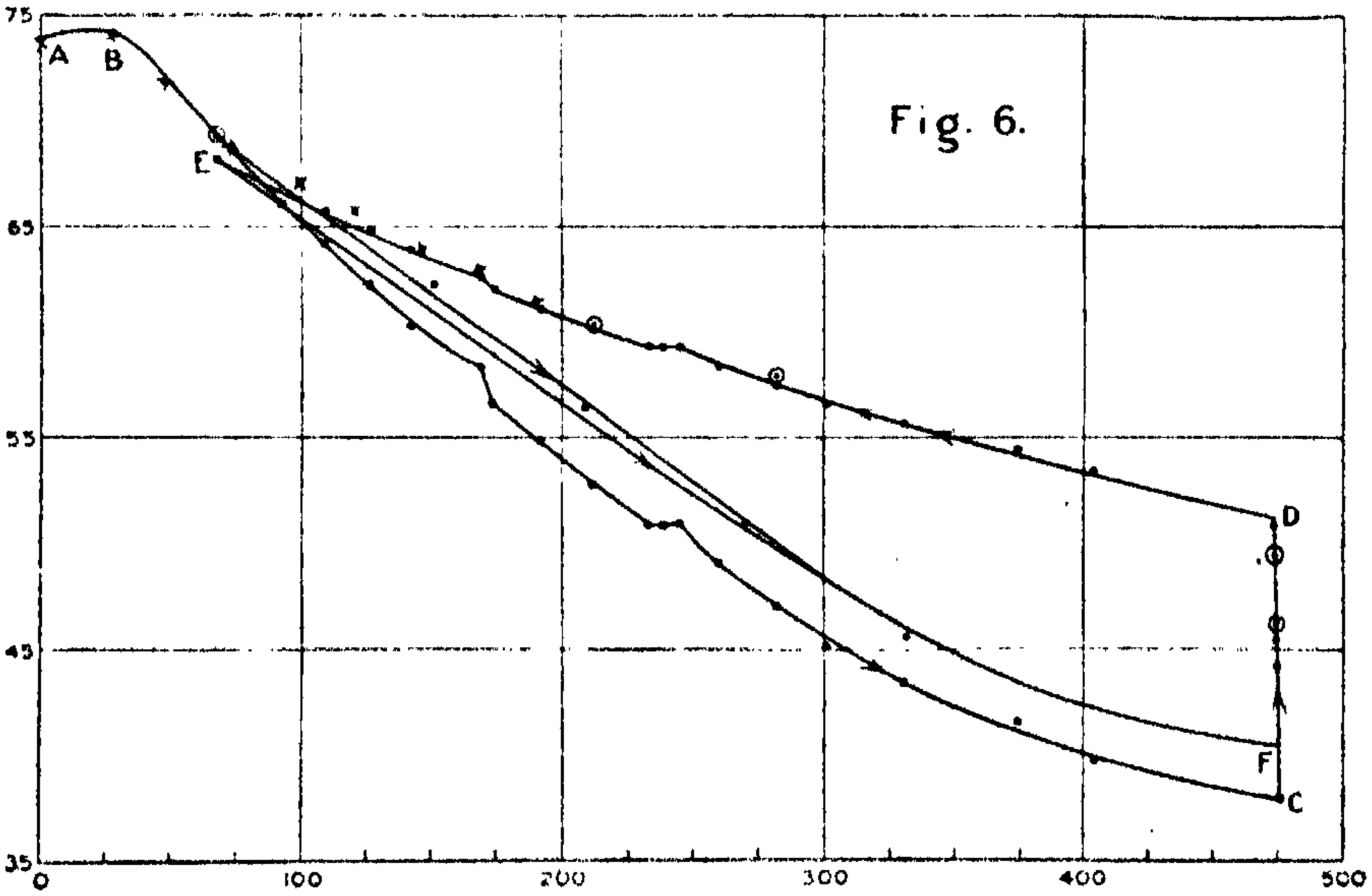


Fig. 5.

Cymene is a relatively inactive substance. With the diminished activity, the sharp points of inflection on the curve disappear, and a curve of gradually changing slope is obtained. The hysteresis is seen in the curve of expansion which follows on and is continuous with the curve of contraction.

Heavy Oil.—From its source may be regarded as being mainly composed of paraffins. The curves for the heavy oil are again those characteristic of an inactive substance. The slope is gradual throughout. The initial rise of tension is well marked.

A surface of clean distilled water was greased by four drops of the oil applied at intervals of 10 minutes. The surface was then allowed to remain quiet for 70 minutes in order, if possible, to attain equilibrium. In all, 4·4 cu. mm. was spread on a surface of 68,000 sq. mm. area. The result was to lower the tension to the first point indicated by a ringed dot (fig. 6). The crossed points refer to an entirely different experiment, in which the disc method was used. The surface was contracted slowly, and the curve AC represents the results. At C it was found that the tension rose when the surface was allowed to remain quiet, and reached a stable point at D; it was then extended rapidly, the points measured being indicated by the ringed dots. It was again contracted, this time rapidly, and now followed curve EF, rising again to D, and again extended slowly, the curve being DE. The whole time occupied in plotting curve DE was 100 minutes, and no sign of variation of tension with time was noticed at any point. The surface was then again expanded along EF. It will be noticed that changes of direction appear at exactly corresponding points in the curve of slow contraction and slow expansion. The four drops of oil spread on the surface do not fuse. The last added drop, after 70 minutes, could be seen by reflected light to form a large patch with sharply defined edges. The surface is therefore composite, and the breaks in the curves may provisionally be referred to this.



The question arises whether the curve of contraction AC would not be identical with the curve ED if time were allowed for the surface to adjust itself after each phase of contraction—expansion of the surface is, so to speak, dead-beat, as is shown by the ringed dots lying on the curve DE of relatively slow expansion. The evidence available does not suffice to settle the point. This, like the many other questions raised, must be made the subject of separate experiment. It may be noticed, however, that the curve of rapid extension of the heavy oil surface coincides with that of slow extension. Also the curve of very rapid contraction EF, which was taken firstly in four rapid stages, and secondly in one jump, *i.e.* in about four seconds, lies above and not below curve EC, which was taken quite slowly, the time occupied in the contraction being about one hour.

A comparison of these results shows that the influence of a substance upon the tension of a water surface is remarkably independent of its own tension, or viscosity. Cymene, a light spirit, has much the same type of curve as that given by an oil so viscous that it will scarcely flow. Benzene, with a surface tension = 28, has relatively little influence on the tension of water. Croton oil, with about the same tension, is incredibly potent. All physical factors have an influence which is insignificant compared to that exerted by the chemical nature of the substance. Organic salts, that is to say the esters, are intensely active, and have sharply inflected curves. Stable substances, paraffins and benzene derivatives, have given curves only slightly inflected, and their activity is relatively slight. The different portions—AB, BC, CD—of the sharply inflected curves I interpret as follows:—AB is the stage in which the layer A is discontinuous. The surface is unstable, and the tension rises above that of pure water when the surface is contracted. In BC the tension is rapidly falling, owing perhaps mainly to the development of a difference of potential between the film A and the water B. That is to say, we may picture partial hydrolysis and ionisation of the ester taking place at the interface. The second inflection at C marks the point at which polarisation is maximal, and from C onwards the tension falls gradually to a minimum. Measurements of tension, however, fail to give the real relation in this region owing to the formation of lenses by condensation of oil on to solid particles. The conclusion that tension falls to a minimum and then rises again is probable from considerations already advanced, and is supported in a remarkable way by the study of the mechanical stability of composite films.

The curves for relatively inactive substances are sharply distinct in type. There is an absence of sharp inflections, and the second inflection may be almost absent. The curve for the heavy oil suggests that the whole effect in reducing tension may be due to an impurity (see p. 632), the bulk of the oil being not relatively but absolutely inactive. The slow decrease in tension with increase in concentration of the substance on the surface of the water I ascribe to the feebleness or absence of chemical reaction at the interface.

The Mechanical Stability of Composite Surfaces.—When a bubble of air is allowed to rise in a fluid the surface is lifted and a film is formed which proceeds to thin owing to the fluid being drained away by its own weight. After a certain time the film becomes so thin as to be ruptured by the tension. The time of persistence of the film obviously will depend upon the viscous resistance to the flow of fluid which thins it, and the speed with which adjustment of tension can be effected by tangential diffusion of the components.* These factors also determine the durability of a flat film. Without attempting precisely to analyse what it means, let us agree to speak of the mechanical stability of a film and to regard the time which elapses between formation and rupture as a direct measure of this property.

Bubbles of the same size were formed as nearly as possible at the same distance (1·5 cm.) below the surface in a trough, and their persistence on the surface measured by a stop-watch. The thickness of the film A was calculated, and the tension measured by the blade method. For each point the duration of at least 10 bubbles was recorded and the mean taken. As the bursting of bubbles on a surface almost invariably raises the tension, this was measured before and after each set of 10, and the mean taken as the tension corresponding to the mean duration. The rise of tension due to the bursting of 10 bubbles corresponds on the average to about 0·05 grm. in the balance pan.

Castor Oil-Water.—The upper curve (fig. 7) is the curve of tension, and the scale of the ordinates appears to the left. The lower curve shows the changes in mechanical stability with changes in thickness of the film. The ordinates for the curve denote seconds and the scale appears to the right. The abscissæ for both curves are to the same scale of $\mu\mu$. The zero of the time scale is the time taken to burst by a bubble formed on a clean surface of water. It is as nearly as can be measured 0·3 of a second. At the second

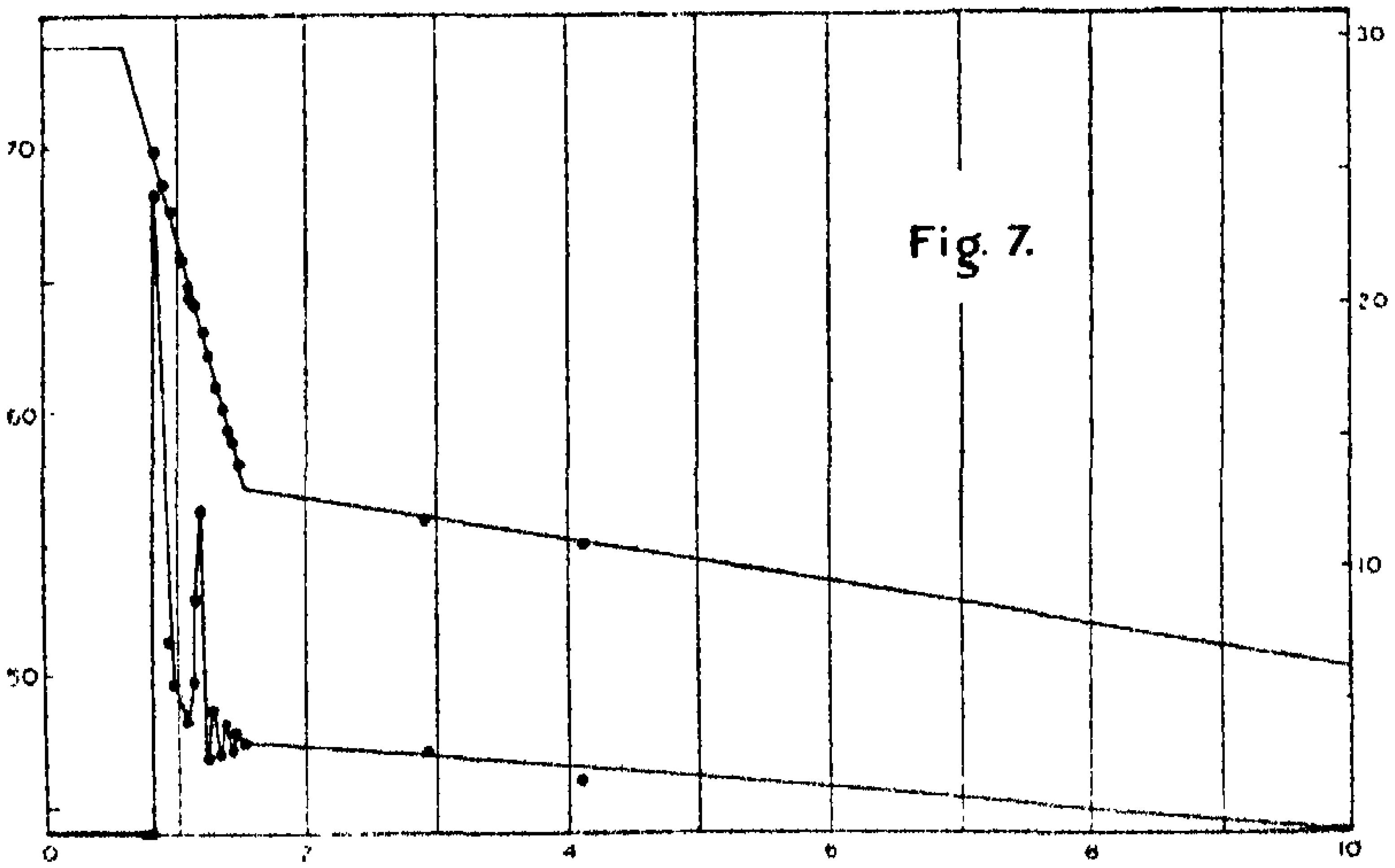


Fig. 7.

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* Gibbs, *loc. cit.*, p. 475.

minimum in the curve the duration of the bubbles is even less than this; I was unable even to estimate it and entered it in my notes simply as 0.

The lower curve shows a remarkable series of oscillations over a region which corresponds to a composite surface whose tension is varying very rapidly. The regular decrease in the amplitude of the oscillations is remarkable. It is obvious that oscillations must occur in the means of any finite series of numbers, for not only is the tension of the surface varying rapidly with variations in the thickness of the film, but also it is subject to large hysteresis effects. Therefore, the durability of a film formed from the same surface will vary with variations in, *e.g.*, the velocity of ascent of the bubbles, the distribution of solid nuclei in the film, etc. The oscillations may, therefore, be a function of the means rather than an indication of a real variation in the mechanical properties of the surface. Their regularity and the orderly decrease in amplitude, however, are most remarkable, and as precisely the same oscillations are found in the longest times and in the means of the longest and shortest times for each set it is, on the whole, probable that they are not merely numerical. Similar oscillations appear in measurements of the mechanical stability of composite surfaces of water with cymene or benzyl cyanide.

In the region of the first oscillation bubbles have sometimes persisted for as long as 70 seconds. It is possible, therefore, that an apex earlier than the one found may be present.

Cymene-Water.—The duration of the bubbles in seconds as ordinates are plotted directly against tension (abscissæ) in the curve (fig. 8). Fewer points

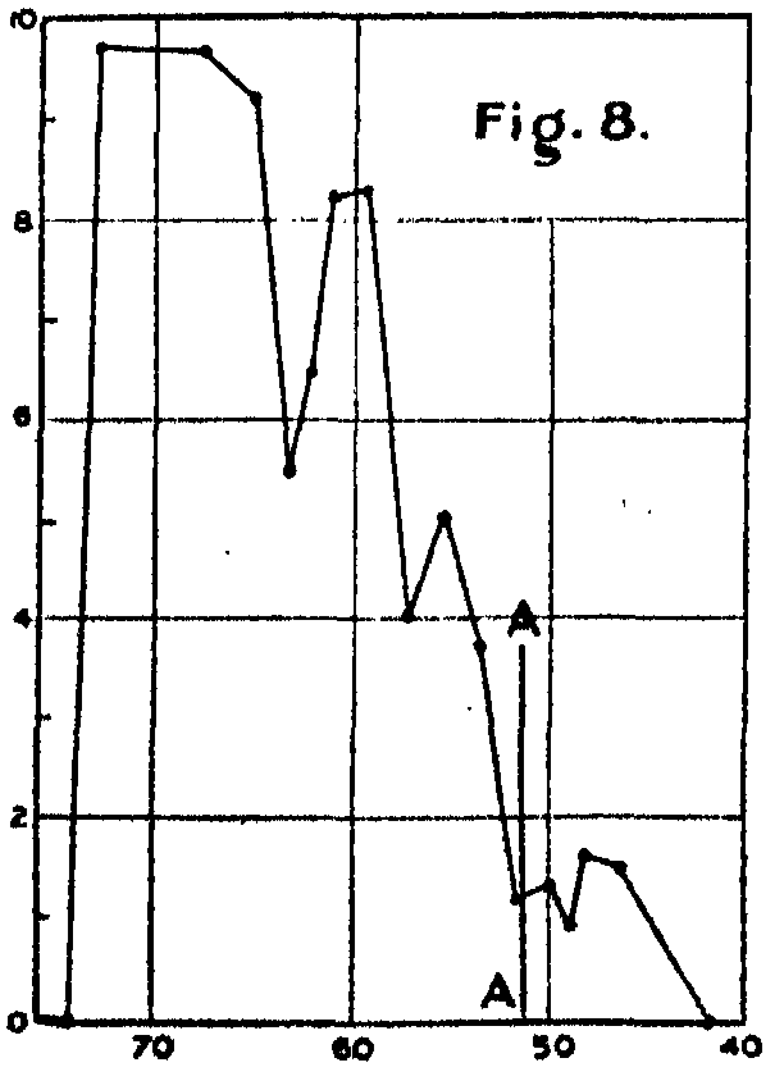

Fig. 8.

were taken, and therefore the true form of the curve probably does not appear. The oscillations are obvious. In both cases there is a stage when mechanical stability is that of a pure surface. It lasts until the tension of the mixed surface begins to fall, with increase in the depth of the layer A. Just after the first inflection of the curve of tension and thickness a film suddenly acquires very great mechanical stability because when it thins, owing to draining away of the fluid, the thinning of layer A, which must also occur, at once raises the tension. When a surface is brought as nearly as possible to the point where mechanical stability appears the record of persistence of bubbles is very remarkable.

Tension.	Duration of a series of bubbles in seconds.
70·1	0·3 0·3 0·3 0·3 0·3 0·3 0·3 21 0·3 0·3 0·3 0·3 0·3 0·3 0·3 0·3 0·3 0·3 0·3 0·3 0·3 0·3 0·3 1 0·3 0·3 15 0·3 0·3 0·4 0·3 0·3
69·7	10 50 55 20 23 22 11 20 22 11

In the first series a few bubbles, so to speak, make films with an order of stability which rightly belongs to the next series. If those bubbles of exceptional structure be disregarded the curve may be said to rise abruptly from the base line to the maximum of mechanical stability.

When the surface of croton or castor oil and water is near this region, bubbles which burst as rapidly as possible give way when the barrier is moved 1 mm. to bubbles which persist for 20 seconds or more and show a full play of Newtonian colours.

It will be noticed that there are two points at which the mechanical stability of the surface is minimal, one when the tension is sensibly that of clean water, and another when it is heavily contaminated. The second minimum occurs when the *mean* thickness of the layer of castor oil is about 13 $\mu\mu$, and of cymene is of the order of 2000 $\mu\mu$. The line AA in fig. 8 marks a thickness of 1980 $\mu\mu$. Beyond this I have no measurements.

Bubbles of the composite surface at the second minimum seem to burst even more rapidly than do those on a clean water surface. In my notes I have simply entered the time as 0. At both minima, and there only, the bubbles burst with a sharp crackle strongly suggesting an electric spark. Some active liberation of energy is needed to account for the rapidity of the rupture at the second minimum. It is not the rate of bursting of bubbles in, *e.g.*, pure castor oil, for that oil is a very viscous fluid. It is a true minimum and beyond it the curve rises again. For instance, a surface was oiled with a large excess of castor oil and the mean duration of the bubbles rose to 3·1 seconds.

The existence of the second minimum of mechanical stability confirms the view already arrived at that between the limiting values $T = T_B$ of a clean surface and $T = T_A + T_{AB}$ of a double surface there is at least one minimal value of T less than either. For let the curves of tension have the form shown in fig. 9. From A to B the tension of a free film decreases as the thickness diminishes, and therefore it is unstable. Also the tension of a free film formed from the composite surface at D would increase with both increase and decrease in thickness; that is to say rupture would occur even more rapidly than in the region AB. But, from considerations already advanced, the extreme range of action of the molecular forces at the surface must be equal to at least half the thickness of the film when T is minimal, and the method adopted for calculating this thickness, which itself gives minimal values, would fix it as 9 $\mu\mu$ for castor oil, and some hundreds of millimicrons for cymene or heavy oil. Are we to conclude from this that the range of the Laplacian attraction really extends to 100 $\mu\mu$ or more? The answer depends entirely upon what is meant by the range of molecular action. If by it is meant the radius of the sphere of influence of a single molecule of, say, a gas, then I think the experiments are compatible with the view that this has an extremely small value, not much greater than the diameter of the molecule itself. Quite another kind of range of molecular action is possible in close packed structures such as fluids and solids, namely a strain transmitted from molecule to molecule.

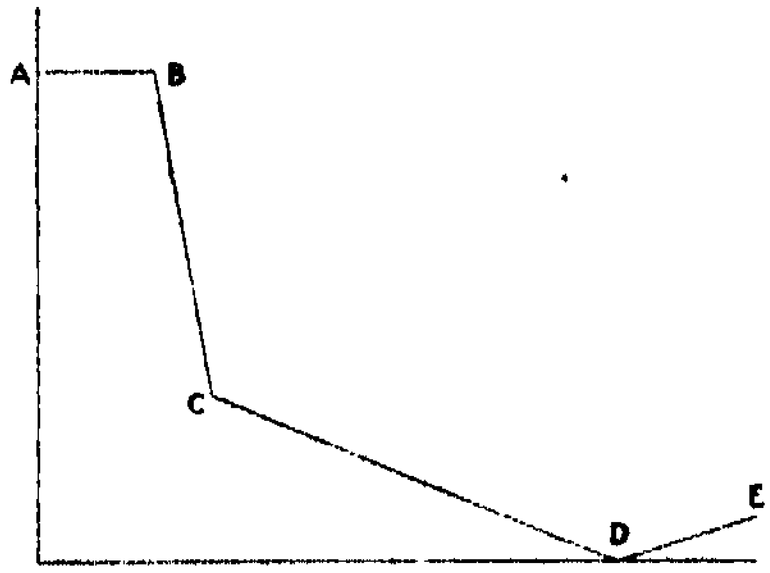

FIG. 9.

At the interface AB, which has sensible thickness owing to the kinetic energy of the molecules, the matter present has to a certain extent the properties of a solid. The stresses are not isotropic, but there is a component along the normal to the surface probably of very great magnitude. This stress may, as we have seen, produce chemical effects, that is to say, it may distort the intra-molecular fields of force, it will also strain the extra-molecular fields. The strains on the intra-molecular fields appear as a partial ionisation of esters, or partial hydrolysis. Looked at from a purely statical standpoint, we may regard these modified molecules as reacting with molecules on *both* sides, and the effect so transmitted from molecule to molecule on each side of the mathematical interface. From the kinetic standpoint we may consider the give and take between these strained molecules and those further away from the interface which must occur in the course of their vibrations. Molecules diffusing out of the interfacial zone are changing to normal molecules, those diffusing in are becoming abnormal, just as at an interface between water and water vapour, vapour molecules entering the zone on the average become polymerised to water molecules, while molecules leaving it to enter the vapour must on the average be in process of depolymerisation. It is this irradiation of strain in a close packed structure which may extend so deeply as to modify the molecular state of a skin some hundreds of microns in depth.

Appendix.—After the foregoing paper was completed, certain new facts came to light which make it possible to extend and confirm the conclusions arrived at. As will be remembered, a suspicion was expressed that the effect of the oil called "heavy oil" upon the tension of water might be due to the presence in it of some active impurity. I wrote to Messrs. Price Patent Candle Co. asking them for information as to the chemical constitution of the oil "Motorine A," and especially whether the distillate I employed under the name "heavy oil" might be taken to be composed entirely of paraffins. I did so because, as the simple paraffins are more stable than benzene, the chemical theory of the tension of composite surfaces demanded that the effect of paraffins upon the tension of water should be even less than that of pure benzene.

The courteous letter which I received from Messrs. Price informed me that the Motorine A contains glycerides, which would account for its activity; further, that my distillate also might contain glycerides, that is esters, or products of the decomposition of glycerides. Messrs. Price sent to me a sample of a paraffin oil about as heavy as Motorine A, and about the same time I came, by accident, across another sample of an oil containing chiefly paraffins. These oils I will call B and C respectively. Both of them refuse completely to spread upon pure water. The statement is founded upon the most rigorous tests I could devise. One experiment was as follows:—The trough and blades were scrubbed with strong caustic potash, and left in running tap water for one hour. The trough was then rinsed out with water freshly distilled in a silver still, filled with water, and the surface scraped at intervals for an hour. It was now not possible to detect any contraction of surface by the movement of motes. Carefully cleaned blades were inserted, and the tension found to be constant when the surface was contracted as much as possible. The barriers were placed at the extreme end of the trough. A very few grains of lycopodium were then dusted on to one spot—very few in order to avoid risk of contamination. While the position of a particular cluster of grains was being observed along a fixed line of sight a small drop of oil B was placed on the surface 1 cm. distant from the cluster. The cluster did not move at all, and the tension did not vary. A tiny drop of oil C was then placed 2 mm. away from the cluster, again with no result. Each drop floated on the surface as a tiny lens. The barriers were now moved, and the surface contracted as much as possible, with no effect upon the tension. In contracting the surface it was noticed that the lenses of oil did not move until they were impelled forward by the upward slope of the surface to the barriers. That is to say, the surface was so pure as to be "non-contractile." They were driven in this way right up to the blades. Both barriers were now lifted out, without any sign of expansion of a "skin," and placed touching one another in the middle of the length of the trough. They were then rapidly moved apart to each end and on to the fresh surface so formed a few grains of lycopodium were placed, and oil drops beside them, all as rapidly as possible. The oil did not spread at all.

The great chemical stability of the paraffins makes chemical interaction with water impossible, and with the absence of chemical action at the interface the term $f(\sigma)$ in equation (11) vanishes, and the term in brackets reduces to $2T'_{ab}$. Some degree of chemical action, therefore, would seem to be necessary to make one fluid spread as a film between two others (air and water). This leads to a purely chemical theory of the miscibility of fluids, for fluids mix when T_{AB} is negative, and given the relation

$$T_{AB} = T_A + T_B - 2T'_{AB},$$

this occurs when $2T'_{AB} > T_A + T_B$, that is, when the energy of chemical action per unit area of interface is sufficient to satisfy the condition

$$2\,[T'_{ab} + f(\sigma)] > T_A + T_B.$$

Oil C is completely colourless and transparent. The contour of the edge of the lens and the nature of the oil-water surface can therefore be followed with ease. Careful examination of the lens shows that the water-air surface is drawn under its edge. The contour of a large flat-topped lens, 2 or 3 cm. in diameter, is somewhat as shown in fig. 10. The significance

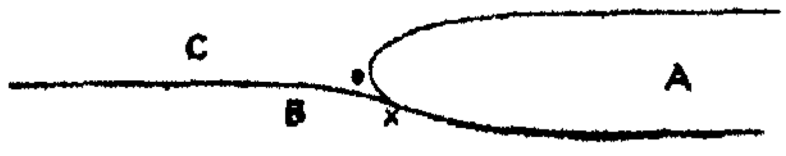

Fig. 10.

of this is obvious, namely, that $t_{AB} > t_{BC}$, for, if the relation be one of equality, the angle θ must be 102° in order to satisfy the relation

$$t_{AC} = 2\,(t_{BC} \cos \tfrac{1}{2}\theta),$$

when $$\frac{t_{AC}}{t_{BC}} \text{ is put } = \frac{T_{AC}}{T_{BC}} = \frac{30}{74},^{*}$$

a relation which is certainly sufficiently exact to prove the proposition. From this point two possibilities confront us: either that at the edge x three fluids do actually exist in contact, in which case Marangoni, Quincke, and Lord Rayleigh are wrong in concluding that Neumann's triangle is necessarily illusory; or that $T_{AB} > T_{AC} + T_{BC}$, in which case the lens of A cannot touch B but is separated by a pellicle of air. The choice between these two alternatives must be based upon a study of the optical properties of the surface. The general appearance of the AB surface does not suggest the presence of a pellicle of air at all.

It is interesting to note that the second alternative may imply a repulsion of A for B. This obviously follows from the relation $T_{AB} = T_A + T_B - 2T'_{AB}$ if the quantities due to air be ignored and T_A, T_B be put respectively equal to T_{AC}, T_{BC}. The quantity T'_{AB} must then necessarily be negative.

The corpuscular theory of matter traces all material forces to the attraction or repulsion of foci of strain of two opposite types. All systems of these foci which have been considered would possess an unsymmetrical stray field—equipotential surfaces would not be disposed about the system as concentric shells. If the stray field of a molecule, that is of a complex of these atomic systems, be unsymmetrical, the surface layer of fluids and solids, which are close packed states of matter, must differ from the interior mass in the orientation of the axes of the fields with respect to the normal to the surface, and so form a skin on the surface of a pure substance having all the molecules oriented in the same way instead of purely in random ways. The result would be the polarisation of the surface, and the surfaces of two different fluids would attract or repel one another according to the sign of their surfaces.

The statement, so commonly made, that a drop of one fluid refuses to spread on the surface of another only when the latter is contaminated by a film of impurity is remarkably far from the truth unless the contamination in question be the air—an interpretation not usually included in the statement. I have found lenses of oil C on pure water unchanged after 24 hours, the edge still being tucked in. The lens, however, at once flattens if the clean

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[*] Quincke's value for the tension of paraffin is 30. My own measurements of the tension of oil C give 30·5 at 12°.

water surface be *very* slightly oiled with an active substance such as castor oil, and the edge takes the form shown in fig. 1. Castor oil reduces the quantity T_{BC}, and therefore the result is at first sight paradoxical. The explanation is simple—I owe it entirely to an observation made by Mr. Stevens. When a coloured body such as impure dibromricinolic acid is used to contaminate the water surface it may be seen to be drawn in as a film under the lens. The quantity T_{AB} is therefore also reduced in value.

An instance of the fact that spreading is made possible, not prevented, by a film of impurity, which must not be too thick, is furnished by oil B, which spreads slowly on tap water but refuses to spread if the surface has been first thoroughly scraped. When a lens of fluid A stands on a surface of water which is coated with a film of A, it is possible that the layer of discontinuity AB of the general surface is continued under the lens. In that case the composite surface between lens and water would be composed of two surfaces of discontinuity of different molecular structure, namely, the surface of mixed oil and water, which is an extension of the general surface, and the surface of the oil.

OBITUARY NOTICES

OF

FELLOWS DECEASED.

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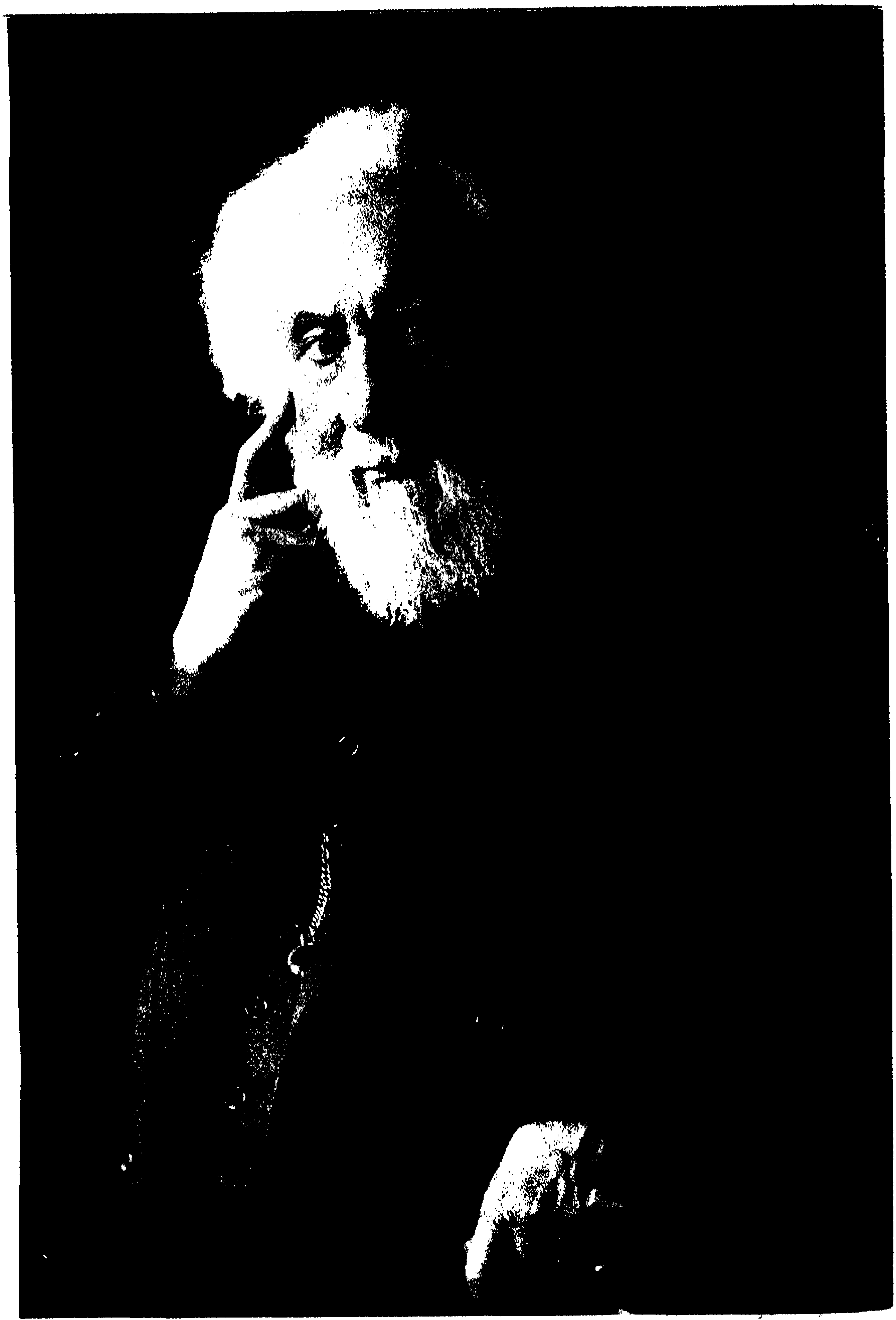

William Huggins.

SIR WILLIAM HUGGINS, O.M., K.C.B., 1824—1910.

By the death of Sir William Huggins on May 13, 1910, the Royal Society lost a past President and one of its oldest and most distinguished Fellows. He was one of the earliest to apply the spectroscope to the analysis of the light of the stars. From the importance and diversity of the discoveries which he made and the methods which he originated, he may with justice be called the founder of Astrophysics. It was his good fortune to assist in and follow the progress of this branch of knowledge for nearly half a century.

William Huggins was born in London on February 7, 1824, his father being in business in the City. He was entered at the City of London School in the first term of 1837, and stayed there till Christmas, 1843. In the school records it is stated that he gave the German Declamation in praise of the founder, John Carpenter, on Friday, July 28, 1843. After leaving school he continued his studies under private tutors, paying attention to classics, modern languages, and Hebrew. After a few years in business he was able to retire and devote his life to scientific pursuits.

In an autobiographical article in the 'Nineteenth Century,' for June, 1897, entitled "The New Astronomy: A Personal Retrospect," he tells us that it was with some hesitation that he decided to give his chief attention to Observational Astronomy. He was strongly under the spell of the rapid discoveries which were then taking place in microscopical research in connection with physiology. He joined the Royal Microscopical Society in 1852, and it was not till 1854 that he became a Fellow of the Royal Astronomical Society. He purchased a house at Tulse Hill, which was then a little distance out of London, and in 1856 built an observatory in his garden, reached by a passage from the house.

The observatory consisted of a dome, 12 feet in diameter, and a transit room. A 5-inch telescope by Dollond, equatorially mounted, and a small transit were the instrumental equipment. At that time a 5-inch refractor was considered a large rather than a small instrument. With the 5-inch equatorial Huggins made observations and drawings of the planets. His earliest published paper contains drawings of Jupiter for October 14 and 15, 1856, and of Mars for April 28 and May 19.

In 1858 he purchased from Mr. Dawes an object glass of 8 inches diameter made by Alvan Clark, the famous founder of the American firm which in later years made the great telescopes for Washington, Lick, and Yerkes. This object glass had met with high approval from Dawes, and no one was more competent to judge than that distinguished observer of double stars, who obtained the name of "eagle-eyed" by reason of the acuteness of his vision. Huggins thus became the possessor of a very fine telescope, which he mounted equatorially and provided with slow motions.

He tells us that he soon became dissatisfied with the routine character of ordinary astronomical work. The belief that the most important and interesting discoveries in astronomy had been made, and that details only required to be filled in, was prevalent in the middle of last century. That this view was entirely erroneous has been proved as regards Dynamical Astronomy by the work of Delaunay, Hill, and others, and as regards Stellar Astronomy by the recent cosmical developments which have their foundation in the accurate measures of the positions of stars.

But neither of these main branches of the astronomy of the period was quite suited to the genius and tastes of Huggins. "Just at this time," he tells us, "when a vague longing after newer methods of observation for attacking many of the problems of the heavenly bodies filled my mind, the news reached me of Kirchhoff's great discovery of the true nature and the chemical composition of the sun from the interpretation of the Fraunhofer lines. This news was to me like the coming upon a spring of water in a dry and thirsty land. Here at last presented itself the very order of work for which in an indefinite way I was longing—namely, to extend his novel methods of research upon the sun to the other heavenly bodies."

Kirchhoff's memoir, in which he demonstrated with full experimental verification the relationship of the dark lines in the solar spectrum to the bright line spectra of the elements obtained in his laboratory, was published in 1859. In the following year, in conjunction with Bunsen, he showed that the sun contained many elements known to exist on the earth. Although the theoretical ideas of Kirchhoff were not so novel as he had thought, having been to some extent largely anticipated as regards the main principles by Stokes and Balfour Stewart, spectroscopy as an important method of research dates from this paper of 1859.

Huggins relates in the 'Nineteenth Century' how, on January 15, 1862, he attended a soirée of the Pharmaceutical Society, and met his friend and neighbour, W. A. Miller, Professor of Chemistry at King's College, London, and Treasurer of the Royal Society from 1860 to 1871. After the soirée the two friends drove back to Tulse Hill together, and Huggins asked Miller to join him in his proposed attempt to apply the method of "prismatic analysis," employed by Kirchhoff and Bunsen, to the stars. Miller at first hesitated, as the small amount of light from a star rendered the success of the experiment doubtful, but finally agreed to co-operate.

Kirchhoff and Bunsen had compared in their spectroscope, simultaneously, the light of the sun with light from various terrestrial sources. But the total light received from one of the brightest of the stars is less than the fraction 10^{-10} of that received from the sun. All the light which falls from a star on an object glass can, however, be concentrated into one point, the telescopic image. A spectroscope had therefore to be designed and applied in such a manner that the whole of this light could be utilised. It was accordingly mounted firmly on the telescope, with the slit at the focus; and the terrestrial light with which comparison had to be made was obtained from the sparks of an induction coil, and was bent round into the tube of the spectroscope by means of a reflecting prism placed over half of the slit. The spectrum of a star obtained in this way was, however, a mere line, too narrow for the eye to detect any lines crossing it. To broaden it a cylindrical lens—an optical appliance then seldom used—was obtained and placed within the focus of the telescope, thus lengthening the point of light on the slit into a short line, and giving the necessary breadth to the spectrum.

By the end of 1862 a stellar spectroscope had been constructed of sufficient dispersive and defining power to resolve such lines as D and *b* of the solar spectrum, and competent to reveal the finer lines in the spectra of the stars if these should be found to resemble those in the solar spectrum This spectroscope utilised two dense flint glass prisms of 60° angle. The collimating lens had a diameter of 0·6 inch and a focal length of 4½ inches, the ratio of aperture to focal length enabling the whole of the light from the linear image of the star on the slit to fall upon the collimating lens. The viewing telescope had an aperture of 0·8 inch and a focal length of 6·75 inches; it was carried by a micrometer screw which turned it so that different parts of the spectrum could be examined, and the relative positions of the lines in the spectrum accurately measured. Particular pains were taken to ensure accuracy in the relative positions of the stellar and comparison spectra. Owing to flexure of the spectroscope the absolute reading of the micrometer was not the same for the same spectrum line for stars at different altitudes. Therefore for each star a preliminary observation was made, which secured coincidence of the comparison spectrum of sodium with that obtained from a small alcohol lamp saturated with sodium chloride placed close to the centre of the object glass of the telescope. It was verified that when this adjustment had been made, lines from other parts of the two spectra also coincided. Thus when for any star the presence of the double line corresponding to D had been satisfactorily determined, it was only necessary in further comparisons so to adjust the spark that the sodium lines from it agreed with these lines from the star.

Besides the points of difficulty which were thus successfully surmounted in the construction of a stellar spectroscope, an additional one arose from the want of convenient maps of the spectra of terrestrial elements. Huggins devoted a large part of the year 1863 to mapping, with a train of six prisms, the spectra of the elements, using as a standard of reference the spark spectrum of air obtained by the discharge of a large induction coil fed by a condenser consisting of nine Leyden jars. In this way maps and tables extending through the whole length of the visible spectrum were made for no less than 24 elements.

A brief note in which diagrams of the spectra of Aldebaran, α Orionis, and

Sirius are described had been communicated to the Royal Society in February, 1863, but it was not until April, 1864, that complete results were communicated. In this important paper ('Phil. Trans.,' 1864, vol. 154, pp. 413—435) the authors state that they have investigated the spectra of fifty stars to a greater or less extent, but have concentrated their efforts in the complete examination of two or three stars. The spectrum of Aldebaran, for example, was compared directly with the spectra of sixteen terrestrial elements, and the existence of sodium, magnesium, hydrogen, calcium, iron, bismuth, tellurium, antimony, and mercury in this star was announced. In Betelgeux they found sodium, magnesium, calcium, iron, and bismuth. The presence of some of these metals has not been confirmed by later work: but these remarkably accurate pioneer researches established beyond question the authors' conclusions that "the stars, while differing the one from the other in the kinds of matter of which they consist, are all constructed upon the same plan as our Sun, and are composed of matter identical at least in part with the materials of our system."

Simultaneously with the appearance of the first announcement by Huggins and Miller of their preliminary results, Rutherfurd published, in the 'American Journal of Science,' an account of a study by very similar methods of the spectra of the Moon, Jupiter, Mars, and several of the fixed stars. He did not, however, pursue this line of research, but turned his thoughts to astronomical photography. The work of Secchi, carried on contemporaneously with that of Huggins and Miller, was complementary to their studies. He investigated and classified the spectra of 600 and later of 4000 stars by the use of a prism placed in front of the object glass of his telescope. This method had been employed by Fraunhofer in very delicate work, before, however, the meaning of the dark lines in stellar spectra named after him was understood; and later, Donati used the imperfect method of a slitless spectroscope. The use of a prism in front of the object glass avoided the observational difficulties with which Huggins and Miller had to contend, and was suitable for the important work of a survey of a large number of stars. The disadvantage of the method is the absence of the fiducial lines which are obtained by the comparison spectrum when a slit spectroscope is used. To interpret stellar spectra with certainty the more laborious method of Huggins and Miller was necessary, more especially in the early stages of the science.

Owing to pressure of other duties, Miller was obliged to discontinue his co-operation with Huggins when their researches had reached this stage. They had worked together from January, 1862, to April, 1864, and in that period had laid the foundations of the methods to be applied in the spectroscopic study of the stars. From this time till his marriage, ten years later, Huggins pursued his researches single-handed.

On August 29, 1864, Huggins made a discovery of cardinal importance. Having pointed his telescope on a planetary nebula in Draco, described in Sir John Herschel's Catalogue as "very bright, pretty small, suddenly brighter in the middle, very small nucleus," he found that the light of the nebula, "unlike any extra-terrestrial light which I have previously subjected to prismatic analysis, is not composed of light of different refrangibilities, and therefore does not form a spectrum. A great part of the light of this nebula is monochromatic, and, after passing through the prisms, remains concentrated in a bright line, occupying in the instrument the position of the part of the spectrum to which its light corresponds in refrangibility." A narrower slit showed two fainter lines in addition. The bright line was found to agree in position with the brightest of the air lines, viz., the strongest line in the spectrum of nitrogen; the faintest of the three lines coincided with the F line of hydrogen, while the third line did not coincide with any known line, but its position was identified by its proximity to a line of barium.

This historic observation proved that the nebula in Draco is not an incandescent solid or liquid transmitting light of all refrangibilities through an atmosphere which intercepts some of them—not a body of the type of our Sun—but is a widely extended mass of luminous vapour. In a moment a definite answer had thus been given to the question whether all nebulæ were aggregations of stars too distant to be resolved into separate units by the telescope, or were, in Sir William Herschel's words: "A shining fluid fit to produce a star by its condensation." By the middle of the nineteenth century many nebulæ had already been resolved into multitudes of stars by the large telescopes which had been directed to them, and it was matter of speculation whether all might not be resolvable with still larger telescopes. Huggins' spectroscope showed that this was not the case, and left tenable the view that nebulæ were "the early stages of long processions of cosmical events which correspond broadly to those required by the nebular hypothesis."

The researches on nebulæ were pursued by Huggins with characteristic thoroughness. Eight other bodies were found to give spectra which indicated their gaseous nature. In all of these the same bright line was found coincident in position with the line of nitrogen, while generally the two fainter lines seen in the Draco nebula were also seen. Six of these bodies were small and comparatively bright objects, designated as "planetary" nebulæ by Herschel. The other two were the ring nebula in Lyra and the nebula in Vulpecula. But the great nebula in Andromeda, and the bright condensation associated with it, did not give a gaseous spectrum like the other nebulæ examined; they gave a continuous one, similar to that shown by a star, though, on account of its faintness, dark lines could not be seen crossing it.

In the following winter the great nebula in Orion was examined, and the same three bright lines found in the spectrum of all parts of that nebula. Its gaseous constitution was therefore established. Observations of Lord Rosse and Prof. Bond were thought to have resolved the great nebula, as well as the ring nebula, into discrete points. If so, these nebulæ must be considered not as simple masses of gas, but as systems formed from the aggregations of such masses around centres of condensation. The four bright stars in the centre of the Orion nebula were also examined; they showed continuous spectra with no indication of absorption lines, and it was noted that the continuous spectrum of the stars in the neighbourhood of the green nebula line was brighter than this line in the adjacent nebula. The existence of the same three bright lines in all nebulæ, indicating an identical gaseous constitution, appeared to show that the nebulæ possessed "a structure and purpose in relation to the Universe, altogether of a distinct and of another order from the great group of cosmical bodies to which our sun and the fixed stars belong." Huggins soon afterwards adopted the view that the gaseous nebulæ were to be regarded as precursors of the stars in the course of evolution of the Stellar Universe.

Leaving on one side speculative questions, he made a more complete examination of the nebulæ and clusters, comparing his results with the telescopic observations made with Lord Rosse's great reflector. By August, 1866, he had examined the spectra of more than 60 nebulæ and clusters. About one-third of these were found to give spectra consisting of bright lines, indicating their gaseous constitution. None of the bodies showing bright line spectra had been resolved into stars by Lord Rosse. On the other hand, all the true clusters, which could be resolved into distinct bright points, gave spectra which were apparently continuous, and, in addition, many nebulæ, of which the great nebula in Andromeda is a striking example, gave spectra of a similar character.

At this stage, subjects for investigation crowded themselves upon Huggins' attention. The regular fluctuation in the brightness of variable stars might be elucidated by spectroscopic examination. If physical changes occurred, they would be shown by changes in the spectra. Again, if diminution of brightness were caused by the interposition of a dark companion, additional lines of absorption might be shown in the spectrum. Observations of Betelgeux at its maximum brightness in February, 1866, showed that a group of lines was missing which had been seen and mapped two years previously. While these observations were in progress a new star appeared in the sky. Such bodies may be considered as extreme types of variable stars. They flash up suddenly and slowly fade. One of these rare phenomena was opportunely observed on May 12, 1866, by Mr. Birmingham, of Tuam, County Galway. He immediately communicated to Mr. Huggins his discovery of a new star of the second magnitude in the constellation of Corona. When the news was received on May 16 the star was of the third magnitude; it was still a bright star and suited to spectroscopic examination. Huggins sent a messenger to Miller and they directed the spectroscope to the new star.

Examination showed the spectrum to be different from any previously examined; and, as described in the 'Proceedings' (vol. 15, p. 146):—"The light of the star is compound and has emanated from two different sources.

Each light forms its own spectrum. In the instrument these spectra appear superposed. The principal spectrum is analogous to that of the sun, and is evidently formed by the light of an incandescent solid or liquid photosphere which has suffered absorption by the vapours of an envelope cooler than itself. The second spectrum consists of a few bright lines, which indicate that the light by which it is formed was emitted by matter in the state of luminous gas." The two principal bright lines were in the positions F and C of the solar spectrum, and showed that the luminous gas consisted in part of hydrogen. Their great brightness was taken as an indication that the gas was hotter than the liquid or solid photosphere of the star. In conjunction with the sudden outburst of the star and its rapid decline in 12 days from the second to the eighth magnitude, these facts suggested that the star had become suddenly enwrapt in the flames of burning hydrogen.

The early researches of Huggins are of such general character as to make an appeal to all who are interested in physical science as well as to astronomers. The observations of the new star astonished a still wider circle, which did not hesitate to conclude that, "from afar astronomers had seen a world on fire go out in dust and ashes." The new star drew attention in a sensational manner to the possibilities of the new science of which Huggins was laying the foundations.

The structure of comets is a subject marked out for elucidation by prismatic analysis. In 1864 Donati found that the comet of that year had a spectrum consisting of bright lines. Huggins examined faint comets which appeared in 1866 and 1867, and was able to detect a very faint continuous spectrum from the coma, from which he inferred that its light was probably reflected sunlight. In the middle of this faint spectrum a bright point was seen, showing that the nucleus of the comet was self-luminous and gaseous. This bright point appeared to coincide with the principal bright line in the spectra of nebulæ, and at first Huggins supposed the lines might have the same origin. Early in 1868 he observed the spectrum of Brorsen's comet, and found it to consist of three bright bands. The transverse length of the bands showed that they did not arise solely from the nucleus of the comet but from the brighter parts of the coma. When the slit of the spectroscope was narrowed the bands did not become sharp, and in that respect differed from the spectra of nebulæ.

The positions of the bands were determined by micrometric measurements, and by comparison with various terrestrial spectra. It happens, curiously, that this earliest obtained spectrum of a comet's head is not of the character usually found in these bodies; but it has recently been pointed out that the spectrum of the tail of Morehouse's comet of 1908 resembles that found by Huggins in the head of Brorsen's comet.

On June 13, 1868, a comet was discovered by Winnecke, with a coma very bright at the centre and suitable for spectroscopic observation. Huggins examined it with a spectroscope containing two 60° prisms, and found that the light was resolved into three bright bands. These bands were brightest on their less refrangible sides, where they commenced sharply, and gradually faded away on their more refrangible sides. They could not be resolved into lines even when a spectroscope of greater dispersion was employed. On the following day the spectrum as drawn and measured was compared with various terrestrial spectra. The positions of the bands, and their general character, resembled the spectrum obtained when a spark is passed through olefiant gas. The next evening a direct comparison was made between the spectra of the comet and of olefiant gas, and the bands were found to agree exactly in position. Later observations have shown that this spectrum of the three bands found in hydrocarbons is characteristic of the heads of comets.

Huggins delivered at the British Association at Nottingham on August 24, 1866, a "Discourse on Spectrum Analysis applied to the Heavenly Bodies." He concludes the lecture by summing up the knowledge which had been gained by the method. This summary serves to show the great discoveries he had made in the few years from 1862 to 1866 and the state of Astrophysics at the time.

1. All the brighter stars, at least, have a structure analogous to that of the Sun.
2. The stars contain material elements common to the Sun and Earth.
3. The colours of the stars have their origin in the chemical constitution of the atmospheres which surround them.
4. The changes of brightness of some of the variable stars are attended by changes in the lines of absorption of their spectra.
5. The phenomena of the star in Corona appear to show that in this object at least great physical changes are in operation.
6. There exist in the heavens true nebulæ. These objects consist of luminous gas.
7. The material of comets is very similar to the matter of gaseous nebulæ and may be identical with it.
8. The bright points of the star clusters may not be in all cases stars of the same order as the separate bright stars.

Observations made later, in 1868, showed the incorrectness of the view (7) that cometary matter was similar to that of the nebulæ. The explanation of the colours of stars cannot now be accepted as complete. With these exceptions the conclusions of this lecture all hold, and are a statement of the important and fundamental knowledge then obtained by the spectroscopic study of the stars.

At the time when he was making simultaneous comparisons of stellar and terrestrial spectra for the determination of the chemical constitution of the stars, Huggins realised that such comparisons might serve to determine the motions of the stars in the line of sight. If the stars were moving to or from the Earth, their motion compounded with the Earth's motion would alter to an observer on the Earth the wave-length of the light emitted by them, and consequently the lines of terrestrial substances would no longer coincide in position in the spectrum with the dark lines produced by the absorption of the vapours of the same substances in the stars. The two-prism spectroscope he employed was sufficient to show that no displacement in any of the stars he examined was so great as the interval between the two D lines, and thus to obtain the important conclusion that none of these stars had velocities to or from the earth amounting to 196 miles per second. From the velocities of the few stars whose parallax was sufficiently well known, it was seen that the order of the quantity to be sought was in their case only a fraction of the interval between the D lines. He therefore designed and had constructed a spectroscope of much greater dispersion, equivalent in power to 6½ prisms of 60°. At the same time he experimented in different ways with a view to making the comparison spectrum more trustworthy and more convenient. Two pieces of silvered glass were fixed before the slit at an angle of 45°, leaving an opening of one-tenth of an inch between them for the passage of the star's light from the object glass of the telescope. The light from an induction-spark whose position relatively to the telescope was kept fixed by careful precautions, was reflected into the spectroscope by these pieces of glass. The star's spectrum was therefore seen accompanied by two comparison spectra, one on each side of it.

In the winter of 1867 he made observations on Sirius, a star which was suitable on account of its brilliancy and of the great intensity of its hydrogen lines. He compared the line at F with the corresponding hydrogen line. At first hydrogen at atmospheric pressure was used, but as the width of the line obtained in this way was greater than the corresponding dark line in the spectrum of Sirius, a vacuum tube fixed in front of the object glass was substituted. The line thus obtained was about one-fifth of the width of the broad line in the spectrum of Sirius, and was seen distinctly as a bright line on the dark line. It was clearly seen not to coincide with the middle of the line, and the distance from the middle was estimated in terms of the micrometer screw. It was found that the displacement towards the red was 1·09 tenth-metres, giving a velocity of separation of Sirius from the Earth of 41·4 miles per second. Allowing 12 miles for the recession of the Earth from Sirius owing to its orbital motion, there remained a movement of recession of 29·4 miles per second of Sirius from the solar system.

The importance of these researches and their extreme delicacy made it desirable that they should be pursued with greater optical power. The President of the Royal Society, in his address for 1869, stated that "the Council have resolved to provide a telescope of the highest power that is conveniently available for spectroscopy and its kindred inquiries. . . . The instrument will be entrusted to such persons as, in their opinion, are the most likely to use it to the best advantage for the extension of this branch of science; and in the first instance there can be but one opinion that the person so selected should be Mr. Huggins."

The Oliveira bequest of £1350 to the Society facilitated this project, and a tender from Mr. Grubb was accepted in April, 1869, for the construction of an object glass of 15 inches aperture and of 15 feet focal length, on an equatorial which could be easily worked by an observer without an assistant. In order that observations on the heat of the stars, which had already been attempted by Huggins, might be pursued, the equatorial, at the suggestion of de la Rue, was also provided with an 18-inch reflector which could be substituted for the 15-inch refractor.

A drum of 18 feet diameter was erected in 1869–70, instead of the 12 feet dome, to house the new equatorial. By February, 1871, the instrument was installed and found to work admirably. Spectroscopes specially adapted for the instrument were constructed suitable for the observation of stars, nebulæ, and the sun.

With this new instrument the determination of velocities in the line of sight was immediately continued. The best means of introducing the comparison spectrum were again considered. Although the reflection from a silvered surface in front of the slit worked well, some troublesome adjustments and a liability to displacement were avoided by a plan adopted instead of it. Holes were drilled in the telescope tube 2 feet 6 inches from the focus, and tubes carrying the vacuum tubes or electrodes were inserted. The spark was in this way brought right into the axis of the telescope.

The following paragraph from a paper presented to the Royal Society in 1872, in which the results of observation of thirty stars are given, may be quoted as showing the great difficulties of these observations and the care bestowed on them by Huggins:—"It may be well to state some circumstances connected with these comparisons which necessarily make the numerical estimations, given farther on, less accurate than I could wish. Even when spectroscope C, containing four compound prisms, and a magnifying power of 16 diameters are used, the amount of the change of refrangibility to be observed appears very small. The probable error of these estimations is therefore large, as a shift corresponding to 5 miles per second (about 1/40 of the distance of D_1 to D_2), or even a somewhat greater velocity, could not be certainly observed. The difficulty arising from the apparent smallness of the change of refrangibility is greatly increased by some other circumstances. The star's light is faint when a narrow slit is used, and the lines, except on very fine nights, cannot be steadily seen, in consequence of the movements in our atmosphere. Further, when the slit is narrow, the clock's motion is not uniform enough to keep the spectrum steadily in view; for these reasons I found it necessary to adopt the method of estimation by comparing the shift with a wire of known thickness, or with the interval between a pair of close lines. I found that, under the circumstances, the use of a micrometer would have given the appearance only of greater accuracy. I wish it therefore to be understood that I regard the following estimations as provisional only, as I hope, by means of apparatus now being constructed, to be able to get more accurate determinations of the velocity of the motions."

Comparison with later measurements has shown, as is not surprising when it is considered that all the apparatus had to be improvised, that the velocities obtained for these thirty stars are, when regarded as standard determinations, of but small weight. Nevertheless, the result of the efforts which Huggins made to determine precise values for the velocities in the line of sight must be considered as a great step in the progress of Astronomy. He attempted a practical problem so novel and difficult that only his appreciation of its great importance could have sustained him in his effort. After the publication of Huggins' paper, line of sight determinations were taken up at Greenwich, and observations were carried on for many years by Mr. Maunder. But it was not till the years 1888 to 1892, when photography was applied by Vogel and Scheiner, that a reliable procedure was evolved.* Huggins had the good fortune to witness that immense development of this branch of Astronomy, in which he was the pioneer, which has been made possible by the great light-gathering power of large telescopes combined with spectroscopes of high resolving power and sensitive modern photographic plates.

The large spectroscope which he had installed in 1867 enabled Huggins to prosecute researches on the Sun. A comparison of the spectrum of the Sun near its limb with that at its centre, and of the spectra of sunspots with the solar spectrum, engaged his attention. He also endeavoured to obtain in direct sunlight by increased prismatic dispersion the spectrum of the prominences which are visible during total eclipses on the limb of the Sun, and in the Report of his Observatory to the Royal Astronomical Society in February, 1868, described fully and definitely the method of observation. In the detection of the spectrum of the prominences he was, however, anticipated by Janssen and by Lockyer. But he had priority a few months later in a new application of the principle that was involved; he succeeded in making an image of a solar prominence visible in each bright line by the simple method of widening the slit of the spectroscope.

In 1875 Dr. Huggins married Miss Margaret Lindsay Murray, in whom he found, to quote his own words, in addition to an inspiring helpmate, an able and enthusiastic assistant. Her name is associated with that of her husband in the authorship of most of the work after this date.

From 1876 to 1880 Huggins was engaged on the application of photography to stellar spectroscopy. So early as 1863 he had obtained a spectrum of Sirius on a wet collodion plate, but did not prosecute researches in this direction, as the plates were not sufficiently sensitive, and their use involved numerous practical difficulties. He saw that the gelatine dry plate, from the convenience attending its use and its great sensitiveness, was well adapted for spectroscopic research. Its reaction to ultra-violet light made it possible for spectra of stars to be obtained in this hitherto unexplored region. But, owing to the great absorption by glass of light of wave-length shorter than the violet, a refracting telescope and glass prisms are unsuitable for work on this part of the spectrum. Huggins therefore decided to use the 18-inch speculum mirror of his Cassegrain telescope and to fit it with a suitable spectroscope. This he constructed of a single 60° prism of Iceland spar, with collimator and camera lenses of quartz. He removed the small convex mirror of his telescope and mounted the spectroscope with its slit at the focus of the 18-inch speculum, 13 feet distant from the eye-end of the telescope. To enable him to bring the star to be observed on the slit, and to keep it exactly there during an exposure which might be of an hour's duration or more, he made the jaws of the slit of speculum metal and maintained the adjustment by watching the reflection of the star-image from the jaws by means of a small telescope mounted in the central hole of the large speculum.

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* H. C. Vogel, "On the Progress made in the Last Decade in the Determination of Stellar Motions in the Line of Sight," 'Astrophys. Journ.,' vol. 11, p. 373.

With this instrument he obtained in 1876, with the assistance of Mrs. Huggins, a spectrum of Vega showing seven strong lines, two of which were known to be due to hydrogen, and the remaining five were continuations hitherto unobserved of the same series of hydrogen lines, which afterwards became classical as the subject of Balmer's law (*infra*). With some minor improvements, observations on the brighter stars were continued in this manner till 1879, when the results were communicated to the Royal Society in a paper on "The Photographic Spectra of Stars" ('Phil. Trans.,' 1880, Part II, p. 669).

Maps and tables of wave-lengths of the lines are given for the white stars Sirius, Vega, γ Cygni, γ Virginis, η Ursæ Majoris, γ Aquilæ, and (a star of different type) Arcturus, extending from H_γ, λ 4340, to λ 3300. The spectra of these white stars were found to possess a remarkable similarity. The photographs showed 12 very strong lines. The first three of these were the hydrogen lines, H_γ, H_δ, H_ϵ. The remaining nine were not coincident with any strong lines in the solar spectrum, but the symmetrical appearance of the whole group suggested at once that all belonged to the spectrum of the same substance. These lines were afterwards obtained in the spectrum of terrestrial hydrogen by Cornu. In 1885 Balmer showed that all were embraced with great exactness in the simple formula $\lambda = 3645{\cdot}6\, m^2/(m^2-4)$ by giving m in succession the values 3, 4, 5, etc. Huggins afterwards obtained spectrographs of stars showing 31 lines belonging to this series with the same exactness; and thus the discovery of the hydrogen series in the spectra of the stars provided the stimulus for the subsequent sorting out of the lines of the spectra of other elements into series which has been effected by Kayser and Runge, Rydberg, Ritz, and other physicists.

Huggins directs attention to three characteristics in these stellar spectra: (i) the differences in width and diffuseness of the hydrogen lines; (ii) the absence or presence of the K line due to calcium and its intensity relatively to the hydrogen lines; and (iii) the number and distinctness of other lines. These features served as a basis for a classification of the stars. In an addendum to the paper, in which spectra of Capella, Aldebaran, and Betelgeux obtained by him in January, 1880, are also considered, he arranges the stars in an order substantially the same as that given by Vogel a few years previously, as indicating successive stages in the evolution of these bodies.

The appearance of a fairly bright comet, in 1881, presented an opportunity for pushing researches on cometary spectra into the ultra-violet region. The spectrum was photographed with the spectroscope he had used for stars, and revealed two strong bright lines at 3883 and 3870, which were identified with two cyanogen lines found by Profs. Liveing and Dewar. There was also a continuous spectrum, in which the Fraunhofer lines were visible, showing that a part of the comet's light was reflected solar light. In the following year he photographed the spectrum of Comet Wells, and found it to be entirely different from the comet of 1881. It consisted of five bright bands, whose positions he measured, but he did not succeed in determining their chemical origin.

In this year he also obtained a photograph of the spectrum of the Orion nebula, and found, in addition to the lines he had observed visually long before, an extremely strong line in the ultra-violet at the approximate wavelength 3730.

In the years 1882 to 1885 a good deal of attention was given by Huggins to the problem of photographing the sun's corona without an eclipse. The photograph of the spectrum of the corona taken by Prof. Schuster in Egypt during the eclipse of May 17, 1882, had shown the coronal light to be strongest in the part of the spectrum from G to H. By the use of screens of coloured glass or liquid Huggins limited the light to this range of wave-length in the hope that this would enable the coronal light to hold its own against the atmospheric glare. He thus obtained photographs which in their general features resembled the corona, and he, as well as other experts to whom the photographs were submitted, thought that a successful start had been made. A resemblance between photographs taken in England near the time of the eclipse of May 6, 1883, and those taken by the eclipse observers in Caroline Island were held to lead to the conclusion that to a distance of 8′ from the Sun's limb the appearances on Huggins' plates were genuine pictures of the corona. A committee was appointed by the Royal Society for the purpose of carrying on experiments under the more favourable conditions provided by high elevation. Mr. Woods, an observer at the 1883 eclipse, was sent to the Riffel Alp at an altitude of 8,500 feet in July, 1884, and took a large number of photographs. Fine matter in the air—due, in Huggins' opinion, possibly to the Krakatoa explosion or else to ice spicules—was always present, and produced sufficient stray light to prevent the experiment being successful. Photographs taken subsequently at the Cape also gave negative results. A final test of the method was made at the eclipse of August, 1886, during the partial phase. In a letter to 'The Times' Huggins says: "The partial phases of this eclipse furnished conditions which would put the success of the method beyond doubt, if the plates showed the corona cut off partially by the Moon during its approach to and passage over the Sun. As the telegrams received state that this partial cutting off of the corona by the Moon is not shown on the plates, I wish to be the first to record this untoward result. I greatly regret that the method which seemed to promise much new knowledge of the corona would seem to have failed." This problem had called for an attack, and the failure of an observer so skilful and persevering shows that a successful result can only be looked for under exceptional atmospheric conditions.

His attention was withdrawn from stellar researches for several years while he was experimenting on the photography of the corona without an eclipse. Some repairs of his instrument were also required. A number of alterations were made, of which the most important was the modification of his equatorial by which it was made to carry both the refractor and reflector instead of only one of them. In addition he constructed a new and more rigid spectroscope for visual observations. In 1888 he resumed observations, both visual and photographic, of the spectrum of the Orion nebula. The visual observations, which were continued to 1890, were concerned with the wave-length and identification of the principal nebular line. The following summary of the history of this line is given by Keeler in the 'Lick Observatory Publications,' vol. 3:—"In 1864 Huggins found that this line coincided in position with the brightest air line, a coarse double, the mean position of which is λ 5003. He then considered that it was probably due to nitrogen; in 1872 with his more powerful spectroscope he gave the wave-length as 5005, and was still disposed to regard it as due to nitrogen, ascribing its displacement to recession of the nebula from the Sun. In 1874 he found that the line was apparently coincident with the less refrangible of the nitrogen lines. He appears by this time to have abandoned his view of the chemical origin of the line. He also discovered a very convenient comparison line in the spectrum of lead. In 1887 Prof. Lockyer, in connection with the 'meteoric hypothesis,' suggested that the nebular line is coincident with the magnesium fluting at λ 5006·4. This rendered the exact determination of the position of the line a matter of great interest. In 1889 Dr. and Mrs. Huggins compared the nebular line with the magnesium fluting, using a very high dispersion. They found the line to be more refrangible than the edge of the magnesium fluting, and to be fine and sharp like the hydrogen lines. They also concluded that neither visual nor photographic observations afforded any evidence of the presence of magnesium in the nebula. In 1890 Prof. Lockyer, from a review of previous observations and his own in that year, maintained that the chief nebular line is a remnant of the magnesium fluting. Dr. and Mrs. Huggins repeated their observations, and confirmed their result that the nebular line is more refrangible than the head of the magnesium fluting." At the request of Dr. Huggins the position of the line was determined by Prof. Keeler, at the Lick Observatory, who found the nebular line to be at λ 5007·0, the head of the magnesium fluting at λ 5007·5, and the two nitrogen lines at λ 5001·0 and λ 5005·3. These observations of Keeler showed conclusively that the nebular line is not a remnant of the magnesium fluting, and its chemical origin is still unknown.

In the 'Proceedings' (1889, vol. 46, p. 40), an account is given of a remarkable photograph of the ultra-violet spectrum of the Orion nebula taken on February 5, 1888. The photograph shows the strong line λ 3727. As the slit was set so that two bright stars in the centre of the nebula fell upon it, the photograph shows the continuous spectrum of these stars as well as the bright line spectrum of the nebula. Four groups of faint lines can be seen extending across the continuous spectra of the stars into the nebula. As the stars have these lines in common with the nebula, the conclusion is drawn that they are not merely in the same direction as seen from the Earth, but are physically connected with it. The photograph was too faint to be reproduced, but was shown to several eminent spectroscopists, who agreed that the appearances on the negative were real lines. In particular, Prof. Hale, in 1894, examined the photograph and verified the existence of the faint lines, and stated that the increase in width and brightness of the lines where they crossed the spectra of the stars was most striking. In the year 1890 the two lines H_ζ and H_η in the hydrogen series were discovered in the spectrum of the Orion nebula, as well as a line λ 3868.

In the same year, on a very clear night in September, Huggins obtained photographs of the spectrum of Vega to determine the point at which the star's light is extinguished by the absorption of the earth's atmosphere. The light was found to be abruptly weakened at λ 3000, but to be faintly seen to λ 2970. Similar results were found from observations of the Sun's spectrum.

In 1890 he discovered a series of six broad lines in the spectrum of Sirius in the extreme ultra-violet from λ 3338 to λ 3199. In the same year he made visual observations of the positions of the bright band in the blue in Wolf-Rayet stars, confirming observations of Vogel's, that this band did not coincide with the blue band due to carbon which is seen in a spirit lamp flame.

The appearance of Nova Aurigæ in 1892 naturally attracted the attention of Dr. and Mrs. Huggins. They observed the remarkable phenomenon that the bright hydrogen lines and some others were doubled by a dark line of absorption on the blue side, and they estimated the relative shift to be 550 miles a second, a result in accord with the estimates of other observers. They also saw in the spectrum the double line of sodium. By comparison with suitable spectra they found that, at this stage of the star's history, there was no sign of the nebular line, and no relationship with cometary spectra. With the ultra-violet spectroscope they obtained a photograph of the spectrum up to the extreme limit which the absorption of the atmosphere permits. It shows the hydrogen series in bright lines, with accompanying absorption lines on the blue side, as well as a large number of other lines. They were unable to examine the spectrum very completely after its remarkable change into that of a planetary nebula in August, announced by Campbell, owing to alterations which were being made in their telescope. A few observations on the character of the bright bands in the positions of the principal and second nebular lines were made by them in February, 1893, and they laid some stress on the difference between these bands and the sharp lines in the spectra of nebulæ.

Huggins favoured some connection between the later stages of new stars and planetary nebulæ. Referring to Nova Persei, the new star of 1901, in his Presidential Address to the Royal Society in that year, he says: "A remarkable phenomenon occurred in Nova Cygni and in Nova Aurigæ, namely, that at a certain stage of cooling, the bright lines peculiar to the gaseous nebulæ (and which are probably due to an undiscovered light substance we may call nebulum) made their appearance, and, together with the lines of helium and hydrogen, which are common to the nebulæ and early white stars, remained to constitute the latest stage of their spectra."

At the very commencement of his spectroscopic work, the Observatory at Tulse Hill was a meeting place where terrestrial chemistry was brought into direct touch with celestial changes. When the spectra of the elements in 1863 were required in order to determine the position of the stellar lines with accuracy, the necessary observations were made by Huggins. In 1870 the spectra of erbia and other earths were examined by him. In 1880 the flame spectrum of hydrogen burning in air was photographed and mapped. Huggins tells us that in the early sixties his observatory had very much the appearance of a chemical and physical laboratory. Throughout his life he excelled in the laboratory experiments which interpret astronomical observations. In 1897 he published a paper "On the Relative Behaviour of the H and K Lines of the Spectrum of Calcium." He wished to elucidate a problem of great interest—why, although in the general spectrum of the Sun there are no fewer than 70 lines attributed to the element calcium, there are only two—the lines H and K—in the spectrum of the chromosphere and in the spectra of some stars. His conclusions were that this was simply due to differences in the density of the calcium in the source from which the light originated. In 1903 he published in the 'Astrophysical Journal' the results of experiments on the modifications in the appearance of the magnesium line λ 4481 under different laboratory conditions of spark discharge, with a view to the interpretation of its appearance in stellar spectra. Still later, when over 80 years of age, he pursued very delicate investigations on the spontaneous luminosity of radium, showing that it was due to phosphorescence of the nitrogen of the air.

The conclusions at which Huggins arrived on the subject of stellar evolution are given in 'An Atlas of Representative Stellar Spectra,' published in 1899. Lady Huggins is associated with Sir William in the authorship of this beautiful volume, and she has enriched it with initial letters and other drawings, which recall the decoration of the works of the old astronomers. A short history is given of the pioneer researches carried out at Tulse Hill, and a description of the various instruments employed. These have been already referred to, with exception of the new ultra-violet spectroscope constructed in 1896. The small spectroscope with its slit in the principal focus of the 18-inch speculum was dismounted and the convex speculum was replaced, restoring the original Cassegrain telescope. The new spectroscope was mounted with its collimator passing through the hole in the large speculum to such a distance that the slit was at the focus of the Cassegrain. The spectroscope consisted of two 60° prisms of Iceland spar, the smaller having a length of 2½ inches and height of 1½ inches. The collimator and camera lenses were of quartz, the latter having a focal length of 15 inches.

The 'Atlas' consists of a series of plates reproduced from spectra photographed with this instrument, extending from λ 4870 to λ 3300. They are of special value as giving many typical spectra over a very long range of wave-lengths. Very little work has been done elsewhere on the ultra-violet spectra of the stars. The text contains a discussion of the "Evolutional Order of the Stars and the Interpretation of their Spectra." In 1879 Huggins had selected as a natural criterion, indicating successive changes of density and temperature, the gradual increase of strength of the calcium line K, taken together with the diminution in strength of the lines of hydrogen and the simultaneous incoming and strengthening of the metallic lines. He thus obtains an order, essentially the same as Vogel's of date 1874, and regards the white stars, such as Sirius, to represent the early adult and persistent stage of stellar life, stars like the Sun and Capella, the condition of maturity and commencing age, while in the orange and red stars, such as Aldebaran and Betelgeux, he saw the setting in and advance of old age. This classification is, in the main, adhered to in 1899. An important addition is the separation of the helium stars from other white stars. From their association with nebulæ they are naturally placed first in the order of evolution. From them the change is continuous to the Sirian stars, from the Sirian to the Solar, and from the Solar to the Red stars.

Sir William and Lady Huggins attach more importance to density than to temperature in causing spectral changes, and they point out how large a part is played by the increase of gravity at the surface which accompanies the contraction of a star. They determine the relative temperature of the stars by the comparative intensities of the ultra-violet and blue portions of their continuous spectra. These delicate observations led to the conclusion that temperatures of stars increase till they have reached the stage of the Sun, and then decrease. Here they are at variance with the conclusions favoured by other astronomers, which make the white stars hotter than those of solar types.

The 'Atlas of Representative Spectra' forms vol. 1 of the 'Publications of the Tulse Hill Observatory.' It was followed in 1909 by vol. 2, containing a collection of Huggins' scientific papers, edited by Sir W. and Lady Huggins, reprinted from the 'Transactions' and 'Proceedings' of the Royal Society and other scientific journals. The Address to the British Association at

Nottingham and the Presidential Address at Cardiff, are also included. The volume contains a reproduction of the portrait of Huggins, painted by the Hon. John Collier during the term of his Presidency, which hangs in the rooms of the Royal Society; it has also a photograph of Lady Huggins. The papers are arranged according to the subjects with which they deal; they present a contemporary record of the growth of Astrophysics in its different branches. In the preface Sir William Huggins says: "Looking back, with the knowledge of the more efficient and perfectly adapted instruments and methods of work which have been gradually introduced during the last forty years, no one can be more conscious than I am of the inevitable shortcomings of my pioneer instruments and methods of work which had to be created under circumstances of no little difficulty. These shortcomings prevented the attainment of accurate results in some single cases, but time has shown that they did not affect the fundamental general correctness of my early work." Huggins witnessed a great advance in Astrophysics. But he saw no departure from the methods he employed. The development was due mainly to an increase in light-grasping power, brought about by large telescopes and sensitive dry photographic plates. Huggins realised clearly what problems could be solved by prismatic analysis, and he showed the right way to set to work. His attack combined a splendid audacity with great judgment. This collection of his papers rounded off the main work of his long scientific life. He relinquished in 1908 the charge of the telescopes and spectroscope which had been placed in his care by the Royal Society in 1871. These were given by the Royal Society on his advice to the Astrophysical Department of the University of Cambridge, and were erected there during his lifetime. Arrangements had been made, at the time of his death, for him to visit Cambridge, to inaugurate the completion of this installation.

Sir William Huggins received many marks of distinction in recognition of his scientific achievements. He was elected a Fellow of the Royal Society in 1865, and received a Royal Medal in the following year. The Rumford Medal was awarded to him, most appropriately, in 1880, and the Copley Medal, the crowning honour at the disposal of the Society, in 1898. The Gold Medal of the Royal Astronomical Society was awarded to him along with Prof. Miller in 1867, and to him alone a second time in 1885. In 1869 he was Rede Lecturer at Cambridge, and he received the honorary degree of LL.D. from that University in 1870. Oxford conferred on him the degree of D.C.L. in 1871, Edinburgh the LL.D. in 1871, Dublin the LL.D. in 1886, and St. Andrews the LL.D. in 1893, and he received degrees from various Foreign and Colonial Universities, including Leyden and Heidelberg. The Paris Academy of Sciences awarded him the Lalande Prize in 1872, and elected him a Corresponding Member in 1874; he also received the Valz Prize in 1883, and the Janssen Gold Medal in 1888. In 1901 he received the Henry Draper Gold Medal from the National Academy of Sciences of Washington.

He was enrolled as honorary or foreign member of most of the principal national learned societies, including the Institute of France, Reale Accademia dei Lincei, the Royal Academies of Sciences of Berlin and Göttingen, the Royal Society of Sweden, the Royal Society of Denmark, the Royal Society of Holland, the (American) National Academy of Sciences, the American Philosophical Society of Philadelphia, and the American Academy of Arts and Sciences of Boston, the Royal Irish Academy and the Royal Society of Edinburgh.

He was created K.C.B. in 1887, on the occasion of the Diamond Jubilee of Queen Victoria. In 1902, when the Order of Merit was instituted by King Edward, Sir William was chosen as one of the twelve who originally constituted the Order.

Sir William Huggins served repeatedly on the Council of the Royal Society. He was three times Vice-President, and in 1900 was chosen to succeed Lord Lister as President. He filled this very important office for five years with marked dignity and distinction. At the suggestion of his colleagues, selections of four of his Presidential Addresses, which treat of subjects of general interest, were published by him in book form. In these he discusses the value of science in education as compared with humanistic studies, considering them as equally essential, and indeed complementary of each other. He also gives an account of the great work that science, as represented by the Royal Society, has done and is doing for the nation.

In 1891 he was President of the British Association at Cardiff.

He served on the Council of the Royal Astronomical Society continuously from 1864 to 1910. He was Secretary from 1867 to 1870, Vice-President from 1870 to 1873, President from 1876 to 1878, and Foreign Secretary from 1873 to 1875 and from 1883 to 1910.

Sir William Huggins gave ungrudging service in all these capacities. Only a week before his death he took part in a meeting of a joint committee of the Royal and Royal Astronomical Societies, for making arrangements for the publication of a collected edition of Sir William Herschel's papers, an undertaking due largely to his initiative. His scientific eminence naturally brought him a great deal of correspondence, to which he gave generously of his time and thought. His unfailing good health enabled him to do this in the midst of his own researches. In the last year of his life he worked for some hours daily in the physical laboratory, spent the afternoon in the study, and wrote in the evening.

His death, at the age of 86, took place in a nursing home in London on May 12, 1910, unexpectedly, after one day's illness.

F. W. D.

GEORGE JOHNSTONE STONEY, 1826—1911.

THE family from which George Johnstone Stoney was derived, on his father's side, settled in Ireland in the seventeenth century, coming from Yorkshire. From the marriage of George Stoney of Oakley Park, King's County, with Anne, daughter of Bindon Blood, D.L., of Cranagher and Rockforest, County Clare, was born in February, 1826, George Johnstone Stoney, eldest son and third child. One other son also was born, Bindon Blood Stoney. The latter, a distinguished engineer, and a Fellow of the Royal Society, died early in 1909. A sister of the late George Johnstone Stoney married her cousin the Rev. William FitzGerald, Bishop of Killaloe, a union which gave rise to the late George Francis FitzGerald, whose remarkable genius, especially in physical science, is known to all. Other distinguished relatives are to be found in William Bindon Blood (mother's brother), who was a professor of engineering and author of professional papers; in General Sir Bindon Blood, G.C.B. (son of mother's brother), Commander of the Forces in the Punjab and distinguished in the Chitral Expedition and in the Boer War; and in Maurice FitzGerald, lately Professor of Civil Engineering in Queen's University, Belfast.

The Stoneys' country property in Ireland was of considerable value during the early years of the last century. Those were times of large profits to agricultural undertakings, the Napoleonic Wars conferring an artificial value on home produce. Irish property fell in value when the wars ceased, and country gentlemen found that encumbrances incurred during the more prosperous times, and as the result of lavish hospitality, were not so easily met as in the good times. Poverty fell upon them and the terrible times of the Irish Famine (1846—48), intensified by the monstrous policy of that day which decreed the local raising of the Poor Law rate just where the famine was most severe, completed the ruin of many Irish families in those districts where the unfortunate tenants stood most in need of the landlord's assistance. The Stoneys' property had to be sold; it fetched about eight years' purchase of the reduced rental, and Johnstone Stoney's widowed mother and her children had no other means.

Many county families who had similarly lost their landed property flocked to Dublin and turned to professional careers in order to make their way in the world. It was a strenuous time in this younger society of Dublin, and one of much mutual helpfulness. Johnstone Stoney and his brother Bindon entered Trinity College, earning the expense of their fees by "grinding," or in English phraseology "coaching." Although unable to afford such assistance for themselves, both brothers had distinguished college careers, Johnstone never failing to obtain a place amongst the first three in the First Class honour lists, and taking a Second Senior Moderatorship in Mathematics and Physics in the Final, the first place going to the

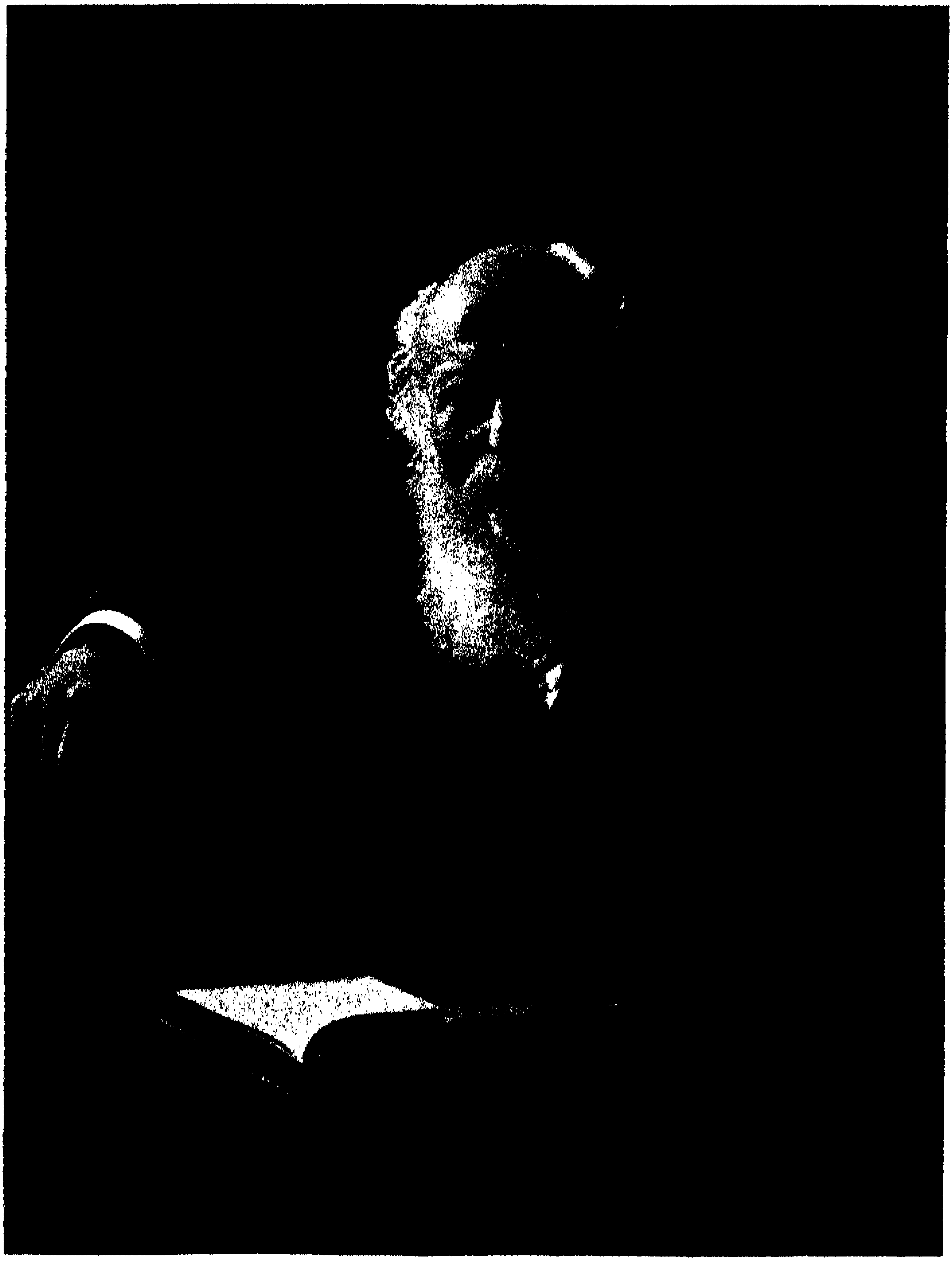

Photo by Miss Edis. 1910.

Grout Sc. et Imp.

G. Johnstone Stoney.

distinguished mathematician Mr. Morgan Crofton, F.R.S. In those days scholarships all went to classical men.

When Johnstone Stoney left college Lord Rosse made him his first regular astronomical assistant at Parsonstown, a post subsequently filled by Robert Ball and by other young men who later on made a distinguished mark in science. Stoney read for the Trinity College Fellowship while at Parsonstown. He entered for it in 1852 and took second place, winning thereby the Madden Prize, which is worth about £300. It was the last examination conducted in Latin, and a wide range of subjects was included in the course, the cumulative marks deciding. Although not so severe an examination as it has since become, the ordeal was a severe one. Stoney was examined in Hebrew, chronology, metaphysics, and classics, besides his own special subjects of mathematics and physics. The range of subjects, the method of cumulative marking, and the encumbrance of Latin as a medium of expression, would handicap any science student. It was, too, an examination in which brilliant originality of mind counted practically for nothing. Stoney is one of many distinguished men whom Trinity College has lost as the result of the exclusively examinational mode of entry to Fellowships.

Johnstone Stoney could not afford to try for the Fellowship again, and Lord Rosse, who was always a true friend to him, used his influence to have him appointed to the Chair of Natural Philosophy in Queen's College, Galway. Stoney remained five years in Galway and then became Secretary to the Queen's University, which brought him back to Dublin and to the wider life of a great University city, a change keenly appreciated by him.

For many years after this Stoney devoted himself enthusiastically to the work of solving the problem of the provincial university, in other words to securing to the local university the same beneficent influence which the greater central universities exert upon those more wealthy students who can afford the cost of residence away from home. The problem was then a new one, for although the older universities have in past centuries gone through times of mere provincial importance, the conditions of their growth and development were different from those which affect a recent institution. The latter has to face at once the rivalry of the older institutions, with their greater prestige, and the facilities of modern modes of travel. In Ireland the whole question is complicated by differences in views as to the mental standpoint of the university, differences founded upon religious principles which seem impervious to argument.

In the midst of these labours, which continued till 1882, when the Queen's University was dissolved, other chances came to Johnstone Stoney, but his devotion to what he hoped would have been his life's work prevented his considering them, though some of these offers would have benefited him pecuniarily and others would have given him greater leisure for research, the latter a condition far outweighing the former in his estimation.

The office of the Queen's University was then situated in Dublin Castle, and Stoney's conversancy with educational matters led to his being frequently consulted by both political parties. He was frequently brought over to the House of Commons, so as to be at hand to give information to the Chief Secretary of the day when Irish educational matters were in question. He wrote many reports on educational subjects, more especially for Sir Thomas Larcom. When Sir Thomas retired, he was anxious that Stoney should succeed him as Permanent Secretary in Ireland. Lord Mayo, then Lord-Lieutenant, sounded him on the subject; however, Stoney frankly told him he approved of Mr. Gladstone's Irish Church Disestablishment Bill as the healthiest policy for the Church itself. This closed the matter, as Lord Mayo was a Conservative and opposed to Mr. Gladstone's policy.

At the request of the Civil Service Commissioners, Stoney added to his other duties those of Superintendent of the Civil Service Examinations in Ireland. The double duties added much to his already heavy office work, and sorely curtailed what leisure he had for scientific work. In 1882 the dissolution of the Queen's University fell as a crushing blow upon Stoney. "At a stroke of the pen, I beheld the labour of nearly thirty years of my life annulled"—in such words he described the event to the present writer. There is no doubt that the policy of dissolution was a most questionable one. The University was dissolved just when becoming most successful. In its stead an examining University was installed, and the several colleges of the old Queen's University became feeders to this institution, which had the power of conferring degrees on purely examinational tests, degrees bearing the same status as those conferred upon students who were not in residence in the colleges. The evils arising, and developing with the lapse of years, in the new Royal University found little defence when, many years later, the latter became the subject of enquiry by the Irish University Commission of 1901. The Commissioners reported that, in addition to defects of organisation, the Royal University "has seriously impaired the value of the University education which was previously in existence. On this side its influence has been one of positive destruction; since it came into being, the growth of the Queen's Colleges has been arrested." In the end, the Royal University, which had supplanted the Queen's, was in turn swept away, and, the present National University of Ireland and the Queen's University of Belfast installed in its place, the purely examinational system being, it is to be hoped, banished for good.

It was during this long period of residence in Dublin that Stoney's influence made itself felt in the policy of the Royal Dublin Society. This Society is unique among voluntary institutions in the United Kingdom—unique in organisation, and, it may be said, unique in the influence it has exerted upon almost every factor tending towards advance of civilisation and national prosperity. Originating in the efforts of a few enthusiasts to better the arts and industries of Ireland, it was founded in 1731, having its first home in Trinity College. Developing year by year, it fostered not only industries but science, and to its inception are due the Royal Botanic Gardens of Dublin, the Royal College of Science, the National Library, the National Museums of Art, Archæology, and Natural Science, and the National Art Gallery of Ireland.

In this Society Stoney served as Honorary Secretary for over twenty years, and afterwards as Vice-President, until he left Dublin for London, on his retirement from official life, in 1893. During his tenure of office the Society went through great and fundamental changes, exacting much extra work from its officers. The Society used to be the channel through which the Government administered grants in Ireland to Agriculture, Science, and Art. The time came when the Treasury felt that it was anomalous for public grants to be administered by a private, voluntary society and out of the direct control of a Public Department. The Royal Dublin Society, in Stoney's time of office as Honorary Secretary, handed over its great collections to the Government, receiving an allotment of capital for the pursuance of its scientific functions, and for enlarging and amplifying its agricultural shows and otherwise helping Irish agriculture. The premises at Ball's Bridge were acquired at this time, and an era of advance in the magnitude and influence of its shows initiated, which has resulted in making them of international importance.

Towards the close of his personal influence in the Royal Dublin Society, Stoney induced the Council to inaugurate concerts directed to the performance of the best chamber music by proficients brought from various parts of the world; these concerts soon became a permanent part of the Society's work, attracting many members to the Society, and undoubtedly doing much for the advance of musical culture in Dublin.

It would be impossible here to estimate adequately Stoney's influence upon the Royal Dublin Society. The work of reorganisation arising in its constitutional changes was enormous. One who, like the writer, served in the secretaryship during more settled times, can realise what it must have been. The Council is a complex body, sitting together as a Council, working apart as three great Committees of Agriculture, of Science and its Industrial Applications, of General Purposes. There are two secretaryships, which generally are regarded as respectively apportioned to Agriculture and to Science. The latter was filled by Stoney, but the secretaries' work is by no means limited by this subdivision. They enter alike into all the questions of public policy continually arising, and into the Financial Committee's supervision of ways and means.

Additional to his general work for the Society Stoney worked wholeheartedly for the advancement of its scientific functions. For many years his own research work was communicated almost exclusively to the Society, and published in its 'Proceedings' and 'Transactions': his aim being to confer upon its publications something more than a local prestige. His gifted relative, George Francis FitzGerald, ably assisted him in this endeavour. The younger men, feeling the advantages of discussions in which men of such critical ability participated, gladly brought their work to the Society, and for many years the evening meetings were characterised by debates of the highest scientific interest. Although the Society still does invaluable work for science, there is no doubt that in the untimely death of FitzGerald, and the loss of Stoney upon his departure to London, the science meetings lost much of their high standing.

The close of his official work in Dublin meant for Stoney a time of leisure; but it came too late for the publication of much of the scientific work he had done. He was then nearly 68 years of age, with health impaired by the long and heavy strain of official work. His life in London was largely devoted to the completion and publication of original work begun in earlier years; but this could only be slowly accomplished, and he died before it was completed according to his wishes.

Stoney's scientific work needs no apology on the score of diversity or of prolificness; but the amount of it conveys but a small idea of his life's work, and, indeed, forms but a small part of it. Only an over-mastering scientific enthusiasm could have elicited such a body of work from a man harassed for the best years of his life by strenuous duties continually leading his thoughts into other channels. Yet a major part of his work was accomplished during those years of official toil. He was a remarkable instance of the resistless power of a great intellectual development; of its relentless pertinacity and resolution. His power of accomplishment was linked with an unusual degree of self-centred devotedness to the immediate subject of his thoughts and speculations. Around this subject the interests of his intellectual life appeared to be gathered and concentrated for the time. With this very conspicuous quality of mind it is the more remarkable that he worked as a devoted and successful official during years of considerable scientific fertility. It must have been a heavy exaction even from one with his high-minded sense of duty. The final facts of his success in both spheres of his work demonstrate at once his intellectual force and his splendid devotion to his aims and to his duties.

One of Stoney's earliest papers was a geometrical examination of the conditions of propagation of undulations of plane waves in media ('Trans. Roy. Irish Acad.,' vol. 24, 1861). The reasoning is mainly directed to explaining why an undulation of the kind considered, when once established, continues to propagate itself in one direction only. Analytical reasoning is not used. Indeed, throughout a major part of his writings Stoney prefers geometrical to analytical reasoning. In a later paper he states his preference for the former: "The chief value of the geometrical form of proof is that it gives us a more continuous view of what is going on in nature, inasmuch as the stages of the geometrical proof of a physical problem keep throughout their whole progress in close proximity to what actually takes place, whereas a symbolical proof is in contact with nature only at its commencement and at its close" ("On a New Theorem in Wave Propagation," 'Phil. Mag.,' April, 1897).

After the appearance of his optical paper of 1861 the subject of geometrical optics does not appear to have enjoyed Stoney's attention till the appearance of the "Monograph on Microscopic Vision" ('Phil. Mag.,' October, November, and December, 1896), that is, till after his official life was closed and he had leisure to work up material which, as in this case, had probably been by him for many years. The study of microscopic vision is based upon a method of resolution into flat wavelets. Stoney shows that the method is one of wide generality, and a series of propositions occupy a large part of the paper, establishing and analysing the fundamental proposition that "however complex the contents of the objective field . . . the light which emanates from it may be resolved into undulations, each of which consists of uniform plane waves," or wavelets, which do not undergo change as they advance. On this basis the causes of the phenomena presented by microscopic vision are sought in a paper ingenious in reasoning and laborious in its scope. The proof of the fundamental proposition given in the first paper did not, however, satisfy Stoney, and several subsequent papers appeared, one criticising an insecure proof advanced by Thomas Preston, "On a Supposed Proof of a Theorem in Wave-Motion" ('Phil. Mag.,' May, 1897); also, on this subject, see 'Phil. Mag.' for February, April, July, and August, 1897, and July, 1898. A proof of the theorem by the principle of reversal is given in a paper published at p. 570 of the 'Report of the British Association' for 1901; and Stoney returns to the matter again in the 'Philosophical Magazine' of February, 1903, this time partly with a view to welcome an analytical proof of the resolution into flat wavelets by E. T. Whittaker. This paper, entitled "How to Apply the Resolution of Light into Uniform Undulations of Flat Wavelets to the Investigation of Optical Phenomena," contains several theorems not contained in earlier papers. All this work was written in ignorance of the fact that Stokes, in one of his earlier papers (1845), had enunciated the same fundamental proposition from which Stoney's work takes origin—but without offering any proof. In a paper contributed to the 'Philosophical Magazine' in April, 1905 ("Flat-Wavelet Resolution, Part III"), Johnstone Stoney announces his discovery of Stokes' priority. It is probable that Sir George Stokes considered it almost self-evident as a general statement " . . . for we may represent an arbitrary disturbance in the medium as the aggregate of series of plane waves propagated in all directions." In an appendix to this paper of April, 1905, Stoney again considers the proof of the theorem, and from a manuscript note inserted in his "Monograph on Microscopic Vision" it would appear that the last mode of regarding the matter was that which he preferred.

Stoney's last published scientific papers were on telescopic vision ('Phil. Mag.,' August, November, and December, 1908), and these are now referred to because they are a continuation of the subject to which Stoney directed his attention early in life—consideration of wave-propagation and the formation of images. In treating of telescopic vision Stoney resolves the light before it enters the telescope into a somewhat special system of undulations of spherical wavelets, *i.e.* into spherical undulations, the centres of which shall be the several points of a plane perpendicular to the optic axis and situated close in front of the objective, and by the interference of which (in the usual manner), at the principal focus, the image is formed; the papers are of the same character—at once ingenious and laborious—as that upon microscopic vision. It is a surprising reflection that Stoney was in his eighty-third year when these elaborate and painstaking papers were penned.

The papers alluded to above represent important work, and are characteristic of Stoney's manner of dealing with investigations of similar description. Their inception dates from the beginning of his scientific career, and they have, therefore, been placed in the forefront of this brief review of his work, but they are by no means the most important part of his work. His investigations in various departments of molecular physics distinctly claim that place.

Stoney's work in molecular physics began in 1860, when, on the basis of Maxwell's estimate of the average length of the free path of the molecules of a gas, he made an estimate of the number of molecules present in unit volume. This was, of course, led up to also by the work of Clausius, and was an early contribution to a great subject, then only beginning to be a subject of research. Waterston's memoir had been submitted fifteen years earlier (1845), and, not being published, the advent of the new ideas had to wait for Clausius' papers of the later years of the forties. For the first time the kinetic theory then received publication, and it was recognised that planetary conditions as regards freedom of motion might attend the movement of a gaseous atom between its encounters. Stoney showed a clear and vivid appreciation of the new molecular science, and from this time forward the application and exposition of its laws occupied him at intervals throughout his life. We gather some idea of the state of the subject by perusing a paper by Stoney appearing in the 'Proc. Roy. Irish Acad.,' vol. 7, 1858. This appears to be his earliest contribution to the subject. We find him demonstrating that the law of Boyle is contrary to the view that the particles of a gas are at rest, or that it can be a continuous homogeneous substance.

Ten years later, writing in the 'Philosophical Magazine' "On the Internal Motions of Gases Compared with the Motions of Waves of Light" ('Phil. Mag.,' August, 1868), we find him complaining that the dynamical theory of gases had not met with the general attention and acceptance which it deserved. In this latter paper a vivid appreciation of the relative magnitudes is shown, and Stoney pictures the source of the light waves as existing in the "from fifty to one hundred thousand of these little orbital revolutions" which the molecules are able to execute between successive encounters. Such thoughts were more fully elaborated later. He closes his review of the subject with his estimate of molecular numbers in a gas at standard pressure and temperature, concluding that in 1 cubic mm. there are 10^{18} molecules.

Arising out of his interest in the kinetic theory of gases are his series of papers on the conditions limiting planetary atmospheres. He first touches on the subject in his paper "On the Physical Constitution of the Sun and Stars," which appeared in the 'Proceedings' of the Royal Society in 1868. In this he infers that a complex atmosphere will, near its outward quiescent boundaries, cease to be homogeneous, the lighter constituents extending further into space. Towards the close of 1870, in a discourse delivered before the Royal Dublin Society, the subject of the absence of atmosphere from the moon is discussed, the conclusion being that the gravitation on the moon will not suffice to retain a free molecule moving in a radial, or even outward, direction, with a velocity of 2·38 kilometres per second. Molecules which occasionally reach this speed may be, accordingly, lost to the moon. A full account of his views is given in his paper "On Atmospheres of Planets and Satellites" ('Trans. Roy. Soc. Dub.,' vol. 6, 1897). Stoney contends that on the earth hydrogen and helium are scarce or absent because of their leakage from the atmosphere; water molecules, on the other hand, cannot attain so great an excess over the velocity of mean square as is required for their escape. The theory has been called in question on deductive reasoning (see papers by S. R. Cook, 'Astrophys. Journ.,' vol. 11, Jan., 1900: and by G. H. Bryan, 'Phil. Trans.,' A, vol. 196, March, 1900). Stoney's argument rests, as he admits, on inductive reasoning, based on the observed facts of the absence of atmosphere from the moon, and the scarcity of helium and hydrogen on the earth, and he meets the deductive objections by questioning the adequacy of the mathematical theory to include all the events which may lead to excessive velocities of isolated molecules in the upper atmosphere. The discussion is too long to enter upon here. In the limit we must accept as true that a small asteroid could not retain an atmosphere by its gravitational attraction; and the view, held by some, of an asteroidal origin of our earth would appear to meet considerable difficulty here, more especially with regard to the existence of the terrestrial hydrosphere. There is no doubt that Stoney's theory removes difficulties in explaining the absence of a lunar atmosphere. It has been applied, too, to the condition apparently obtaining on Mars. However, it must be admitted that other causes may exist to account for the condition obtaining in those bodies.

The discovery by Crookes that a blackened vane suspended in a high vacuum is repelled by radiant heat or by light led to various suggestions as to the cause of the phenomenon. Stoney offered an explanation in harmony with the various experimental conditions which have to be fulfilled in order for the Crookes force to be developed. The theory of Stoney is given, in a somewhat crude state, in the 'Phil. Mag.' for March and April, 1876. Stoney's view may be summarised in the statement that for a certain distance in front of the heated vane, and reaching from it to the glass envelope, when the vessel is not too large, the molecular motions of the rarefied gas are polarised by the thermal conditions, and interpenetrate one another in a degree greater than prevails elsewhere in the gas. The greater molecular interpenetration in the line between glass and vane involves nothing of the nature of a wind, but determines a greater stress in the direction of polarisation. Errors in the earlier statements of his views are corrected in his paper in the 'Trans. Roy. Soc. Dub.,' 1878, and republished in the 'Phil. Mag.' of December, 1878; and a mathematical expression for the Crookes stress is given, based upon an investigation of Clausius of the stress across a layer of gas conducting heat normal to a heater and cooler. FitzGerald took a part in the discussion (*cf.* his 'Collected Papers') by showing that the stress parallel to the heater and cooler could not be the same as the perpendicular stress—or, in other words, a polarisation stress must exist ('Nature,' vol. 17, p. 514)—and by a mathematical discussion of the subject in the 'Trans. Roy. Soc. Dub.,' 1878.

In 1874, in a paper 'On the Physical Units of Nature,' read before the Belfast meeting of the British Association, Stoney pointed out that, on the basis of Faraday's law of electrolysis, an absolute unit of quantity of electricity exists in that amount of it which attends each chemical bond or valency. This paper was printed afterwards in the 'Phil. Mag.' for May, 1882. He suggests that this might be made the unit quantity of electricity. He subsequently suggested the name *electron* for this small quantity. Von Helmholtz, in 1881, independently, drew attention to the existence of such definite elementary charges, which behave like atoms of electricity. Stoney estimated the magnitude of the electron in 1874, finding it to be equal to the unit (then the ampère) $\times 10^{-20}$. This is the same as 1 C.G.S. electrostatic unit $\times 3 \times 10^{-11}$. In this estimate he avails himself of his determination of the number of molecules present in 1 cubic mm. of a gas at standard temperature and pressure, viz., 10^{18}. That the result should suffer from the errors in the then available data detracts nothing from the merit of Stoney's performance. It was pioneer work in an obscure and difficult line of research.

The conception of one or more unit charges of electricity within the atom was soon applied by Stoney to the phenomena of spectral dispersion. Maxwell's ideas on the electromagnetic nature of light were first published in 1862 and 1866, but the final statement of his theory only appeared with his great work on 'Electricity and Magnetism' in 1873. In Stoney's first paper, which deals with the "Internal Motions of Gases compared with the Motions of Waves of Light," which appeared in the 'Philosophical Magazine' for August, 1868, no reference to Maxwell's views is made, nor is there, of course, any suggestion of the electronic origin of light waves. The aim of the paper is to point out that there must be periodic motions within the "molecule" to occasion the spectral lines, motions distinct from those translatory ones which are affected by the temperature of the gas. The latter are irregular, the former are in general regular, save at the instant of collision—an instant short in comparison with the time occupied in describing the mean free path. The causes of continuous and band spectra are referred to. The nature of the internal motions must differ in different gases. A further step is taken in his paper of January, 1871 ('Proc. Roy. Irish Acad.'). The internal atomic motion is a complex periodic motion which, however, is resolvable into harmonics. If we assume the undulation arising in the ether to consist of periodic plane waves, then, whatever its form, it may be regarded as formed by the superposition of simple pendulum vibrations, one of which has the full periodic time, while the others are harmonics of this vibration, which may be developed by Fourier's theorem. While these component vibrations are superimposed in free ether, on entering a dispersive medium the several vibrations no longer keep together, and a physical resolution is effected in the spectrum. Hence simply harmonic sequences of spectral lines would arise from the distinct motions in the molecule of the gas, for there may be several such motions, each producing its own series of harmonics. Applying these views to the case of the ordinary hydrogen spectrum, Stoney finds that the lines *h*, F, and C are nearly the 32nd, 27th, and 20th harmonics of a fundamental vibration whose wave-length *in vacuo* is 0·13127714 of a millimetre, this agreeing closely with Ångström's measurements. A few months later, Stoney, in conjunction with Emerson Reynolds, advances yet further, finding a serial relationship, of the kind referred to above, in a large number of lines in the absorption spectrum of chlorochromic anhydride. But the general result as to the existence of simple harmonic relations was challenged by Schuster and others, on the ground of the theory of probabilities, the instances being held to be too few to establish a case. It was some years later that the observations of Huggins upon stellar spectra led to an extension of the hydrogen spectrum, as this had been observed in solar light; and in 1885 Balmer showed that a comprehensive law for the whole system of hydrogen lines was expressible in a single formula of quite different type; and a train of ideas was thus introduced, which has led to much subsequent work directed to the sorting out of related series in the lines of a spectrum.

Stoney, in his principal paper on this subject ('Trans. Roy. Soc. Dub.,' vol. 4, May, 1891), states his electronic theory of the origin of the complex ether vibrations which proceed from a molecule emitting light. The paper is "On the Cause of Double Lines and of Equidistant Satellites in the Spectra of Gases." His theory is based on the electromagnetic theory of light, and refers a series of spectral lines to the periodic motion of an electron in the atom or molecule, the elliptic partials into which this motion may be resolved by Fourier's theorem accounting for the several lines. If perturbing forces exist an apsidal motion may affect the elliptic partials, and Stoney shows that, while the undisturbed orbit will in general be such as to give rise to a definite series of single lines in the spectrum, the consequences of an apsidal motion affecting some, or all, of its partials is to cause the corresponding lines of the series to become double. He deduces, on these views, the result that the double D lines of sodium in the solar spectrum might be accounted for by the motion in each molecule of an electron in an elliptic orbit having an axial ratio lying between 11 to 1 and 13 to 1, round which ellipse the electron revolves 169,637 times in a "jot" of time, the ellipse being slowly shifted round with an apsidal motion which carries it once round while the electron performs 1984 revolutions. Similarly, precessional motion will occasion triple lines. The "jot" of time is the time light takes to traverse one-tenth of a millimetre *in vacuo.*

A very large amount of work has been done by mathematical physicists within recent years on theories of atomic structures involving the electron in motion; and, again, the importance of the electron in views on the phenomena of the vacuum tube, and on radioactivity, is known to all. Atomistic ideas as to the nature of electricity were, of course, held before Stoney's views were expressed, but there was a period when the continuous theory had largely displaced the atomistic view. This seems to have arisen mainly from Maxwell's teaching. The more recent and, it must now be admitted, more helpful atomistic theory, in its modern development, dates back to the finding of the electron in Faraday's law of electrolysis by Stoney and Helmholtz; and Stoney's use of the electron in a light-giving atom is one of the earliest developments, showing the availability of the conception of a small discrete particle of electricity. This, in the present writer's opinion, is Stoney's most important work for science.

It may be that a very different conception of intra-atomic structure will ultimately prevail, but the moving electron as a constituent part has not as yet found a good substitute. The phenomena of radioactivity have strongly confirmed it. The early work of Thomas Preston on the Zeeman effect also confirms it. Such recent views as those of Ritz, on atomic structure and the explanation of the Zeeman phenomena, assume, indeed, other sources of action and reaction within the atom, but the electron still remains as generator of electromagnetic waves. And even if the electron ultimately yields place to new conceptions it has helped to forward investigation in many lines of research, and those who first gave it to theoretical science have taken a worthy part in the advance of man's knowledge of Nature. The early date of Stoney's work and the clearness and the fullness with which he urged his views certainly entitle him to a leading place among those pioneers.

Stoney gave much time and thought to the subject of the units of physical science and their nomenclature. He served upon the Committee of the British Association for the selection and nomenclature of dynamical and electrical units in 1873—a committee whose recommendations have been very generally accepted. His paper "On the Physical Units of Nature," which was read before the Belfast meeting of 1874, has already been referred to. In it he urges the claims of "the single definite quantity of electricity" observed in electrolysis as a unit of electrical quantity. The paper is printed in the 'Proceedings' of the Royal Dublin Society, 1881. Several other papers relating to the subject of units came from his pen, and throughout his many papers bearing on other subjects he frequently suggests new departures in nomenclature. Indeed, it may be said that his desire for the perfection of brevity and reasonableness introduces some difficulties in the study of his papers, seeing that in some cases an unwonted nomenclature has to be first acquired. His services to the subject of physical mensuration have, however, been great; and till quite late in his life he laboured to facilitate the introduction of the metric system into this country.

The circumstances of Stoney's early life led, as has been mentioned, to his appointment as observer to Lord Rosse at Parsonstown. The interest in astronomy then aroused remained with him throughout life. He wrote both on the instrumental equipment of observatories and on the objects of the heavens. Thus there are papers "On Collimators for Adjusting Newtonian Telescopes" ('B. A.,' 1869); "On the Equipment of the Astrophysical Observatory of the Future" ('Monthly Notices,' 1896); "On the Mounting of the Specula of Reflecting Telescopes" ('Proc. Roy. Soc. Dub.,' 1894). His other papers are principally upon the Leonids. In one of them, a discourse before the Royal Institution (1879), the idea of comets capturing meteorites in virtue of the retardation experienced by the latter when passing through the gaseous substance of the comet is put forward (see also 'Monthly Notices,' June, 1867). Other papers are upon the physics of the solar atmosphere; one of them has already been referred to, another was published in the 'Philosophical Magazine' of December, 1868.

In 1888 Stoney entered upon a study of the numerical relations of the atomic weights. An outline of his results appears in the 'Proceedings' of the Royal Society, April, 1888. The full paper has not been published. The leading idea is that if a succession of spheres be taken whose volumes are proportional to the atomic weights (" atomic spheres "), and the radii of these spheres are plotted on a diagram as ordinates, and a series of integers as abscissæ, a logarithmic curve, $y = \mathrm{K} \log (qx)$, is developed which, in the belief of the investigator, shows that the atomic weights follow laws which can be represented as the intersection of two definite mathematical curves; implying that two definite laws of nature have to be coincidently fulfilled for an atom to come into existence. The curve so represented passes nearly through the positions given by observations. The discussion as to how to reconcile the curve with the slight perturbations, and why neighbouring logarithmic curves pursuing courses close to the observed positions are excluded, occupies several sections of the paper. He also gives a polar diagram in which the radii of the atomic spheres are used as radii vectores. This diagram suggested to him, in the first instance, the logarithmic spiral. The diagram is of much interest, and finds publication in the 'Phil. Mag.,' September, 1902. The quadrants of the figure are alternately found to include electro-positive and electro-negative elements. An unoccupied sesqui-radius appears in the diagram at a place where alone an *abrupt* transition from the electro-positive to the electro-negative character is observed. The inert gases discovered some years later now occupy this radius. In the 'Phil. Mag.' of September, 1902, Stoney suggests that the unusual chemical behaviour of these new elements is a consequence of their occupying a position between the halogen radius, in which the electro-negative condition attains its greatest intensity, and the radius containing lithium, sodium, potassium, rubidium, and cæsium, which are the most electro-positive of the elements. The prediction of missing elements on the indications of the logarithmic law is notified specially by Stoney in a letter to the 'Phil. Mag.,' October, 1902. He suggests here that the new elements will possess the greatest atomic volumes among the elements in the solid state. The specific gravity in the solid state of these bodies has not as yet been determined.

There is no doubt that the logarithmic curve given by Stoney is suggestive in the highest degree, and is a most interesting contribution to this subject. Stoney had the matter very much at heart, and the non-appearance of his full paper evidently caused him much pain. Stoney believed that a mistaken view was taken of what he really aimed at, this belief being supported by a note of Sir George Gabriel Stokes appearing in 'Stokes' Scientific Correspondence,' vol. 1, p. 219. In the month of March, 1911, Stoney, then upon his death-bed and already worn with many months of illness, dictated a memorandum on the mathematical principles which influenced him in his work upon the logarithmic law of the elements. There is no sign of failing power in this memorandum. Extracts from the original manuscript were in consequence made by Lord Rayleigh, and were communicated by him and published in the 'Proceedings' of the Royal Society (A, vol. 85, p. 471, July, 1911). In these extracts the spiral curve is again reproduced.

A considerable number of scientific subjects, additional to those already referred to, engaged Stoney's attention at various times. They range over a wide field of scientific enquiry and often show much originality. In the 'Phil. Mag.' for April, 1890, he suggests that bacteria may derive a part of their life-energy by relations towards the faster moving molecules in the surrounding medium, of a selective nature, so that they escape the second law of thermodynamics much as the Maxwell demon might have done. A very different topic is "The Magnetic Effect of the Sun or Moon on Instruments at the Earth's Surface" ('Phil. Mag.,' October, 1861); also "On the Energy Expended in Driving a Bicycle," in conjunction with his son, Mr. G. Gerald Stoney, F.R.S. ('Trans. Roy. Dub. Soc.,' 1883); Address to the Mathematical and Physical Section of the British Association, 1879; "On Denudation and Deposition" ('Phil. Mag.,' April and June, 1899), etc.

Johnstone Stoney served on several Committees of the British Association. His name appears in Reports on Solar Radiation, Catalogue of Spectral Rays, on papers connected with Spectrum Analysis, 1881; and he acted as reporter of a lengthy compilation of the Oscillation-frequencies of Solar Rays, 1878.

The subject of Ontology engaged his attention for a considerable time; a paper "On the Relation between Natural Science and Ontology" was communicated by him to the 'Proceedings' of the Royal Dublin Society in 1890. This paper is in the highest degree characteristic at once of Stoney's mental attitude towards Nature, his methods of logical analysis, and the tendency he so often shows of a desire to build up a subject in its entirety and from first principles, framing for the purpose new words and new definitions. As already remarked, the tendency to revising the ordinary use of language so as to give it more direct significance and more convenient form often imposes some labour upon his readers. The ontology paper is a really profound and exhaustive review of the subject, and indicative of keen introspection, but it is difficult reading on account of the large amount of definition which the writer deems essential. A second part of the essay was published in 1903 by the American Philosophical Society. An earlier allied essay is "On how Thought presents itself among the Phenomena of Nature," being a discourse delivered before the Royal Institution, February, 1885. A few papers on what may be called abstract physics may be mentioned here: "Survey of that Part of the Range of Nature's Operations which Man is Competent to Study" ('Proc. Roy. Soc. Dub.,' 1899); "On Texture in Media and on the Non-existence of Density in the Elemental Ether" ('Proc. Roy. Soc.,' 1890); "Curious Consequences of a well-known Dynamical Law" ('Proc. Roy. Soc. Dub.,' 1887), etc.

Stoney was keenly alive to the charm and refining influence of music, and, as already stated, did much for the study of music under the auspices of the Royal Dublin Society. He wrote a paper "On Musical Shorthand," and in the same volume (1882) of the 'Proceedings' of the Royal Dublin Society is one on methods of dealing with echoes in rooms. In 1883 he suggests, in the same journal, a mode of prolonging the tones of a pianoforte.

Enough has now been said with reference to his scientific work to show how wide in scope it was. Stoney wrote on other subjects, however: "On the Demand for a Catholic University" ('Nineteenth Century.' February, 1902): and in the interests of his University, he writes upon the subject of its reform in 1874, and speaks in its defence against the legislation which threatened it in 1907. As late as 1910 he printed a thoughtful pamphlet on "The Danger which in our Time threatens British Liberty."

No man ever lived more completely and devotedly for his ideas than did Johnstone Stoney. He was the type of the philosopher. Nothing could check his ardour for research; no labour was too great for him to undertake in the pursuit of his ideas. In spite of heavy office-work which afforded none of the long-vacation leisure of university life, in spite of the absence of that stimulus which comes from a professional scientific life, Stoney published two or three papers each year. Through his middle life he rose at five o'clock in order to get in some scientific work before starting for his office. He was never a very strong man, and this necessitated much restraint as to evening society functions. His Sundays were largely devoted to experiments or writing. His annual holiday was usually for the ten days of vigorous intellectual life of a British Association meeting. At all times he greatly grudged the time and labour of writing down and putting through the press work which had been a pure delight to carry out.

Of the moral attributes of Johnstone Stoney it is impossible to speak without a feeling of profound respect. His fearless love of truth was bound up with an ideal rectitude of life. He stood above all creed that could not appeal to the rationality of man and that denied the continuity of Nature's laws. Intellectually superior to most men, he was yet at once too great and too benevolent to criticise the littleness of the many, the shallowness of their minds, and the fallacies of their tenets. This did not arise in abstraction from the struggle of life and its troubles, for no more sympathetic and kindly man ever breathed. He championed every earnest effort, more especially endeavouring to forward the interests of the younger scientific men with whom he came in contact, in this respect meting to others that same treatment which he himself received at the hands of his early and life-long friend, the Earl of Rosse. Stoney's word was a law to him: what he promised he performed. This is a moral quality which soon gets known, and confers a just influence upon its possessor, not only with those who also possess it, but again with those deficient in it. When Stoney left Dublin, and the occasion was taken by the Royal Dublin Society to present him with a memento of his work for the Society, and again when he received their Boyle Medal, the recognition of his high moral qualities was in the minds of all, and could not be kept out of analyses which were intended to embrace only his social and scientific work.

George Johnstone Stoney received many distinctions during his long and laborious life. Probably the one he most highly valued was the receipt of the first Boyle Medal from the Royal Dublin Society. The medal had just been founded to commemorate the great Irishman who had so large a share in the initiation of the parent scientific society of this country. It was felt by the Council of the Royal Dublin Society that Stoney, above every other Irishman then living, merited the distinction of having his name placed first upon the roll. It was conferred upon him in 1899. He was a Foreign Member of the Academy of Science at Washington, and of the Philosophical Society of America founded by Franklin. He was a corresponding member of Sci. di Lettere ed Arti di Benevento. He was President of Section A at the meeting of the British Association in 1879. He served as Vice-President of the Royal Society under Lord Lister, and also served upon the Council, 1898—1900.

Stoney married his cousin Margaret Stoney. He leaves two sons and three daughters. His eldest son has risen to distinction as an engineer, having been collaborator in the development of the steam turbine with the Hon. Sir Charles Parsons, K.C.B., F.R.S., and is now manager in the Parsons Turbine Works. One daughter is a Lecturer at the London School of Medicine for Women, and another daughter is a London physician. George Johnstone

Stoney died in the eighty-sixth year of his age, on July 5, 1911, after a long illness. His body was cremated, and his ashes buried in the graveyard of the little suburban town of Dundrum, Co. Dublin.

In stature, he was tall; in bearing, dignified; and his features and expression revealed at once his intellectual power, his nobility of character, and his kindly and sympathetic disposition. The portrait prefixed to this memoir was taken in the year 1910, in the eighty-fifth year of his age. It is in every way faithful and excellent.

J. J.

OBITUARY NOTICES

OF

FELLOWS DECEASED.

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GIOVANNI VIRGINIO SCHIAPARELLI, 1835—1910.

GIOVANNI VIRGINIO SCHIAPARELLI was born at Savigliano, in Piedmont, on March 14, 1835: he graduated at the University of Turin in 1854, and studied the practice of astronomy at Berlin Observatory between the years 1856 and 1859, when Encke was the Director. After spending a short time at Pulkowa under W. and O. Struve, he returned to Italy in 1860 to take up the position of assistant to Carlini in the Royal Brera Observatory of Milan, where he spent the remaining years of his life, succeeding Carlini as Director in 1862. He held this position for thirty-eight years, and was succeeded on his retirement in 1900 by Prof. Celoria.

Schiaparelli early proved his mettle by discovering the minor planet Hesperia in 1861, when such a discovery was still something of an event but his first great work was the recognition that meteors were distributed along definite orbits, and that these orbits coincided with those of known comets. He observed that the meteors which occur in greater or less force annually from August 6 to 12, radiated principally from points in the constellation Perseus, and that those which did so possessed a distinctive character of their own, showing that they belonged to a single family. Such a fact is geometrically sufficient to determine the plane and perihelion of their orbit if the eccentricity or period of revolution is assumed, and this determination showed an agreement which could not be accidental with the orbit of the comet I of 1862.

A more signal instance was supplied in 1866, the year of the great shower which radiates from γ Leonis. This orbit proved to be identical with that of Tempel's Comet II of the same year. For this striking discovery the Paris Academy of Sciences awarded the Lalande Prize to Schiaparelli in 1868, and the Royal Astronomical Society its Gold Medal in 1872.

The Brera Observatory was provided with an 8-inch equatorial telescope by Merz,—the same aperture as that which Dawes had used for his valuable maps of Mars in 1864. A comparison of what we owe to that keen-sighted observer with what Schiaparelli afterwards accomplished with equal optical aid is a searching test and proof of the latter's skill. When he turned his attention to the surface of Mars, he completely transformed our knowledge of the face of that planet. Beginning with the opposition of 1877, he followed it on successive occasions up to 1890, producing more and more detailed maps and masses of observation. The later ones were made with a more powerful telescope, by the same maker, of 19 inches aperture. The whole series of measures and observations are wonderfully voluminous as well as delicate, and they are eminently reliable. It may be said that all that Schiaparelli delineated has been in one way or another confirmed.

On Proctor's map, which was based upon Dawes' observations, a few long dark bands leading from the "seas" were shown and were named by him "inlets." Schiaparelli added a host of finer ones, making an irregular meshwork over the whole of the "continents." In describing them he translated "inlet" by "canale," and so introduced, apparently by accident, a term whose artificial implications have served as the channel of so much speculation as to the state of Mars. He showed further that the "canals" and other delicate features were not fixed like the features of the moon, but were subject to fluctuations relatively to one another, and independently of the conditions of vision. Sometimes they were strongly marked, sometimes invisible, sometimes narrow and dark, sometimes broad, sometimes doubled.

Schiaparelli always guarded himself carefully from countenancing any theoretical conclusion as to the nature of these markings. In his latest memoir but one he speaks of them as "the lines (or so-called canals)," and refers to an earlier statement where he tentatively attributes the duplication to some unknown atmospheric cause.

Schiaparelli turned his attention to the surface of Mercury in 1882, and to that of Venus in 1890, and came to the conclusion—as to the former planet, one now generally accepted—that each rotated as the moon does about the earth, so that it always turned the same face to the sun. He was also an excellent and very industrious observer of double stars. He published in 1903, after his retirement, a work entitled "L'Astronomia nell' Antico Testamento," in which he showed the same industry and acuteness that he brought to observation, coupled with a singular wealth of learning. It has been translated into English and German.

He was elected a Foreign Member of the Royal Society in 1896. He died on July 4, 1910.

R. A. S.

JACOBUS HENRICUS VAN'T HOFF, 1852—1911.

Jacobus Henricus van't Hoff was born at Rotterdam on August 30, 1852, his father being a physician of that city. After having received his school education in Rotterdam, he entered the Polytechnikum at Delft in 1869, where he completed the ordinary three years' course in technology in two years. In 1871 he entered the University of Leiden, passing the "Kandidatsexamen" of that university in 1872. Attracted by the fame of Kekulé, he went to Bonn in the same year to study organic chemistry. During these "Wanderjahre" he also spent a short time in the laboratory of Wurtz in Paris. Returning to Utrecht to continue synthetical organic work under Mulder, he obtained on December 22, 1874, the degree of "Doktor der Wis-en Natuurkunde," with a research on cyanacetic and malonic acids.

But already in September, 1874, van't Hoff had laid the foundation of his reputation by the publication of a short pamphlet in Dutch, in which he unfolded his views on the extension of structural chemical formulæ to three-dimensional space, and on the relation between optical activity and chemical constitution. The time was ripe for such a development. Pasteur, in 1861, in his classical 'Leçons sur la Dissymétrie Moléculaire,' had shown the connection between optical activity and hemihedral crystalline form, and had perceived that, in the two isomeric optically active forms, the molecules must possess an asymmetric structure similar to that of object and mirror-image. In fact, Pasteur had suggested that the atoms surrounding the carbon atom might possess a tetrahedral arrangement in space. But it was the work of Wislicenus on the lactic acids which chiefly influenced van't Hoff. The fundamental discovery of the latter lay in the recognition of the part played by the so-called "asymmetric carbon atom," that is, a carbon atom united by its four valencies to four different groups or atoms. Van't Hoff showed that optical activity, and the existence of two optically active isomers, differing merely in the sign of their rotations, only occurred when such an asymmetric carbon atom was present. Very similar ideas were published by J. A. Le Bel, quite independently of van't Hoff, two months later, namely, in November, 1874; but van't Hoff discussed the "geometrical" isomerism in the case of unsaturated compounds more fully than Le Bel.

In 1875 he published a much enlarged French edition of his original pamphlet, with the title 'La Chimie dans l'Espace,' whilst a German edition, with a preface by J. Wislicenus, appeared under the title 'Die Lagerung der Atome im Raume' in 1877. Van't Hoff's views were violently attacked by Kolbe, then Professor of Chemistry at Leipzig. But, in spite of much early opposition and neglect, the new point of view gradually triumphed. The warm support of Wislicenus, and the work of himself and his school, largely contributed to this consummation. Thus was born the now flourishing science of Stereochemistry.

In 1876 van't Hoff was appointed to the post of Docent in Physics in the State Veterinary School at Utrecht. During this period he occupied himself with a number of problems in organic chemistry, many of them relating to points connected with his new theory. As a result of his studies on the nature of the carbon atom and its compounds, there appeared (1878 and 1881) his highly original 'Ansichten über die organische Chemie,' in which he strove after a systematic arrangement of carbon compounds according to their structure, and emphasised the importance of studying chemical reactions from a kinetic point of view. Although preceded here by such pioneers as Harcourt and Esson, and Guldberg and Waage, he developed in the 'Ansichten' the fundamental equations of chemical kinetics and equilibrium on the basis of the law of mass-action.

In 1878 van't Hoff was appointed Professor of Chemistry, Mineralogy, and Geology in the newly created University of Amsterdam. Together with a number of pupils, he now began to develop with extraordinary insight and experimental skill the field of research already indicated in the 'Ansichten.' Starting with the object, "connaître les grandeurs précises et caractéristiques nécessaires pour comparer les propriétés chimiques d'un corps avec sa formule de constitution," he was led step by step to a complete and precise formulation of the velocity and course of chemical reactions and the influence of temperature thereon. At the same time, he applied the laws of thermodynamics with great success to the problems of chemical equilibrium and affinity. The first fruits of these labours appeared in book form in his classical 'Études de dynamique chimique' (1884). In the first section, van't Hoff gives a systematic account of the principles of chemical kinetics, with many new applications to special problems, and a new and important method of determining the number of molecules taking part in the reaction which controls the speed. The second section deals with the application of thermodynamics to chemical equilibria. The notion of "condensed systems" (in which none of the phases possesses variable composition) and the corresponding equilibria at definite temperatures (transition-points) are here clearly enunciated and experimentally treated. The distinguishing feature of this part is, perhaps, the clear and simple exposition of the relation between the change of internal energy of a reaction and the variation of the equilibrium-constant with temperature. This led van't Hoff to his "Principe de l'Équilibrie Mobile," which states that a rise (or fall) of temperature will displace the equilibrium in such a way as to favour that system whose formation is attended with an absorption (or evolution) of heat. This theorem may be regarded as a special case of a more general principle developed by Le Chatelier in the same year (1884).

In his discussion of these matters, van't Hoff showed in a masterly manner how the approximate validity and real practical value of Berthelot's principle could be reconciled with the accurate deductions of thermodynamics.

The third and perhaps most original part of the 'Études' deals with the definition and measurement of chemical affinity. Van't Hoff proposed to measure the affinity with which substances combine or react by means of the (maximum) work obtainable when the reaction is conducted isothermally and reversibly. He showed how this work could be calculated not only from measurements of osmotic and gaseous pressures, but also from the electromotive force of reversible galvanic cells, thus, together with Helmholtz, laying the practical foundations of the newest chapter of modern electro-chemistry, namely, the electrometric measurement of the affinity of chemical reactions. In 1896 the 'Études' was published in a revised and much extended form by E. Cohen, one of van't Hoff's most distinguished pupils, under the title 'Studien zur Chemischen Dynamik.'

Already in 1884 van't Hoff's mind was busy with the idea of osmotic pressure. As he has himself related, his attention was drawn to the osmotic measurements of Pfeffer by his colleague, de Vries, Professor of Botany at Amsterdam. It occurred to van't Hoff that by the use of semi-permeable "osmotic" pistons he could apply the methods of Carnot to solutions. The important question then arose as to how the osmotic pressure was related to the temperature and concentration of the solution. The data of Pfeffer showed that for dilute solutions of cane sugar the osmotic pressure was very approximately equal to the pressure which the cane sugar would have exerted if it could have occupied as a gas the same volume at the same temperature.

Such was the origin of van't Hoff's famous "Theory of Solutions" (1886). But in order to include electrolytes he was obliged to introduce certain coefficients (i), the general equation taking the form $PV = iRT$. As is well known, these i-coefficients have received, in the case of dilute solutions, an interpretation by means of Arrhenius' theory of electrolytic dissociation.

In this way van't Hoff was enabled to work out a simple method of applying the laws of thermodynamics to many important problems, such as the relations between the freezing-point and boiling-point of dilute solutions and the corresponding molecular concentrations, the law of chemical equilibrium and its variation with temperature, the variation of solubility with temperature, etc. These investigations not only provided a sure basis for the methods of determining molecular weights in solution, but gave a great impetus to the study of chemical reactions and chemical equilibrium in (dilute) solutions. Van't Hoff's work was of the greatest influence in the development of the theory of electrolytic dissociation and modern electrochemistry. Although preceded here by Gibbs and Helmholtz, he worked out the fundamental relationship between the equilibrium-constant of a chemical reaction and the electromotive force and concentrations of the constituents in a reversible galvanic cell in which the same reaction occurs.

During the period 1887—1895 van't Hoff published a considerable number of papers dealing with various points connected with his theory of solutions and its relation to the then rapidly developing theory of electrolytic dissociation. One of the most interesting and original of these, entitled "Über feste Lösungen und Molekulargewichtsbestimmung an festen Körpern"

(1890), opened up a new field of research. During the same period van't Hoff, together with a number of his pupils, was actively engaged in the investigation of the conditions determining the formation and decomposition of double salts. These researches were published in collected form in 1897 with the title 'Vorlesungen über Bildung und Spaltung von Doppelsalzen.' His treatment of the subject is characterised from the theoretical side by the application of thermodynamics, and from the experimental side by the elegant methods—microscopic, thermometric, dilatometric, tensimetric, and electrical —which he and his pupils worked out for the determination of the transition-points of the systems investigated.

As may be judged from the foregoing very brief survey, the eighteen years, from 1878 to 1896, during which van't Hoff held the Professorship of Chemistry at Amsterdam, were years of fertile and many-sided research. After having refused several other calls, he accepted, in 1895, an invitation from the Prussian Academy of Sciences, who had elected him a member, to go to Berlin and establish a research laboratory there. He went to Berlin in 1896, becoming at the same time a Professor of the University. There, in collaboration with his old pupil, Meyerhoffer, and assisted by a small number of research students, he began that great series of investigations on the formation of oceanic salt deposits (with special reference to the salt beds at Stassfurt) which occupied him for more than ten years and inaugurated a new era in the study of experimental mineralogy. These researches were a logical outcome of the theoretical and experimental methods summarised in the 'Bildung und Spaltung von Doppelsalzen.' Van't Hoff's method consisted in determining the fundamental non-variant equilibria (consisting of vapour, solution, and three solid phases) which characterise a four-component system at each particular temperature. In this way he succeeded in systematically mapping out the whole region of investigation, so that the amount and nature of the various substances which can crystallise out under given conditions could be deduced. The results of these investigations were published in collected form with the modest title 'Zur Bildung der Ozeanischen Salzablagerungen' (in two volumes, 1905 and 1909).

The last few years of van't Hoff's life were clouded with illness, his lungs having become affected. But in spite of weakness due to the progress of the disease, and of enforced rests in sanatoria, he continued his scientific work. In his last laboratory, set amongst the pine trees of the royal demesne of Dahlem, between Berlin and Potsdam, he had planned and already begun an investigation of the action of enzymes, when death overtook him. He died at Steglitz on March 1, 1911.

During his residence in Berlin van't Hoff found time to publish in book form the lectures which he delivered at the University, with the title 'Vorlesungen über Theoretische und Physikalische Chemie.' The short series of lectures which he delivered in 1901 at the University of Chicago, on the occasion of the decennial celebrations of its foundation, were published with the title 'Acht Vorträge über Physikalische Chemie' (1902). Both these works are characterised by remarkable breadth of outlook, combined with extreme conciseness of statement and close relation of theory to experimental results.

During his lifetime van't Hoff was the recipient of scientific and academic honours from all parts of the world. In 1888 he was elected an honorary Foreign Member of the Chemical Society of London. A similar honour was conferred on him by the Royal Society in 1897, and by the Physical Society in 1911. In 1889 the German Chemical Society, and in 1895 the German Bunsen Society elected him to honorary membership. He was the recipient of the Davy and Helmholtz medals, and of the Nobel prize for chemistry (1901). The Emperor of Germany conferred on him the Order "Pour le mérite," whilst honorary degrees were received from the universities of Cambridge, Chicago, Greifswald, Heidelberg, Manchester, and Utrecht. The thirty-first volume (1899) of the 'Zeitschrift für physikalische Chemie' (of which journal he had been joint editor since its foundation in 1887) was dedicated to him by his pupils in honour of the twenty-fifth anniversary of his promotion to the degree of Doctor.

In 1878 van't Hoff married Miss Jenny Mees, of Rotterdam, who survives him. By her he had two sons and two daughters, all of whom are living.

In his manner van't Hoff was simple and homely. To those who had the privilege of working with him he was endeared by the unaffected friendliness and sincerity of his nature. As a lecturer he made no pretence of oratorical brilliance. He was content to give his hearers an unadorned though profound and fundamental account of the development of chemical facts and theories. As an investigator he will ever be remembered as a great and outstanding genius. Although preceded by many great pioneers, such as Harcourt and Esson, Guldberg and Waage, Horstmann, Gibbs, Kirchhoff, Kelvin, Helmholtz, etc., it was van't Hoff who so developed and systematised chemical dynamics and thermodynamics, that he may well be regarded as one of the chief founders, if not the chief founder, of modern physical chemistry.

Regarding nature with the delicate and finely attuned perception of genius, he saw in chemical reactions phenomena whose course was subject to exact law, and whose limits were controlled by the play of affinities that could be measured and compared. The influence of his work extends far beyond the ordinary bounds of chemistry. Physiology and biology, dealing with the mysterious mechanism of living matter, in which dilute solutions, semipermeable membranes and subtle chemical affinities play an important part, have received a powerful stimulus. A new vista of possibilities has been disclosed to geology and mineralogy. Everywhere the influence of van't Hoff's work has led to advance in the direction of quantitative relationship, to a profounder perception of causality in the sequence and balance of chemical phenomena.

F. G. D.

JOHN ATTFIELD, 1835—1911.

JOHN ATTFIELD was born in August, 1835, near Barnet, in Hertfordshire, the son of John Attfield, surveyor, of Whetstone. The name—originally At-the-fields, and later Atte Felde or Atefeld—is purely English, and it is therefore easy to trace the descent of John Attfield from the John Atefeld who flourished in "the Ville of Staundon" (now Standon, eight miles north-east of Hertford) as far back as 1361.

Attfield was educated at the school of the Rev. Alexander Stuart, then of Barnet, where he developed a taste for scientific pursuits as a direct result of the teaching he received. Having expressed a desire to be allowed to continue his studies in chemistry and physics, he was apprenticed, at the age of 14, for five years to Mr. William Frederick Smith, a pharmacist of Walworth. During the last year of his apprenticeship, 1854, he attended the School of Pharmacy of the Pharmaceutical Society in Bloomsbury Square, and obtained the first prizes or medals in all subjects—namely, chemistry, pharmacy, materia medica, and botany. He passed the Minor or qualifying examination of the Society in the same year, and offered himself as a candidate for the Major examination, but was refused admission, as he was not of age. In September, 1854, he obtained the position of junior assistant to Dr. Stenhouse, F.R.S., lecturer on chemistry in the medical school at St. Bartholomew's Hospital, and subsequently became demonstrator of chemistry at the same hospital. Stenhouse was succeeded by Dr. (afterwards Sir Edward) Frankland, and Attfield remained with the latter as demonstrator, assisting him in research work, besides lecturing at the Addiscombe Military College, until 1862, when he was appointed director of the laboratories of the School of Pharmacy of the Pharmaceutical Society, and afterwards Professor of Practical Chemistry, which subject was given up by Prof. Redwood so that he might devote all his attention to the teaching of theoretical chemistry and pharmacy.

Shortly after his appointment Attfield went to Tübingen, where he obtained the degree of Doctor of Philosophy, presenting as his thesis a paper on "The Spectrum of Carbon," read before the Royal Society in June, 1862. Attfield remained Professor of Practical Chemistry at Bloomsbury Square till his retirement from public life in 1896.

He was elected a Fellow of the Chemical Society in 1862, and was a member of Council during the period 1874–8; was a Fellow, one of the founders of, and for several years a member of Council of the Institute of Chemistry; was elected a Fellow of the Royal Society in 1880; was an honorary member of the Pharmaceutical Society of Great Britain, and of some twenty other pharmaceutical colleges and societies all over the world.

Attfield was no less active in private than in public life; he took a keen interest in educational, philanthropic, social, and recreative movements in general, and was one of the leading spirits in the Herts Natural History Society and in the Watford Fieldpath Association. He retired practically from all public work in 1896; and, although suffering under rather severe physical disabilities, he was able to enjoy life in a very quiet way, his garden and his books being specially a great solace to him. He died at Ashlands, Watford, on Saturday, March 18, 1911.

Attfield's published work deals almost exclusively with scientific pharmacy. During the time he was at St. Bartholomew's Hospital he wrote most of the chemical articles in 'Brand's Dictionary of Art, Science, and Literature,' and in the Arts and Science Division of the 'English Cyclopædia,' and he also found time to revise and extend the chemical portion of the fourth edition of Clegg's work on 'The Manufacture and Distribution of Coal Gas.' His first original paper, "On the Solubility of Mercurial Precipitates in Alkaline Salts," was read in November, 1859, to the Chemical Discussion Association of the Pharmaceutical Society, and was published in the 'Chemical News' for 1860. From that time till 1897, he contributed between seventy and eighty papers to pharmaceutical and scientific literature.

In 1867 appeared the first edition of Attfield's 'Manual of Chemistry: General, Medical, and Pharmaceutical,' the basis of the work being some manuscript notes which the author had prepared for the students at St. Bartholomew's Hospital. The book has now reached its nineteenth edition.

Undoubtedly the greatest work of Attfield was in connection with the 'British Pharmacopœia.' It is interesting to note that the name Johannes Attfield appeared in the prefatory pages of the 'Pharmacopœia' of 1677, and of the reprints of 1678 and 1682, as one of the Fellows of the College of Physicians responsible for the production of the volumes, and he appears to have belonged to one and the same family as the editor of the 1898 'Pharmacopœia.' On the appearance of the 1864 edition of the 'Pharmacopœia,' lectures were given at Bloomsbury Square by Profs. Bentley, Redwood, and Attfield, which with other criticisms aided in the suppression of the book and the appointment by the General Medical Council of Prof. Redwood and Mr. Warrington to edit a new edition. Redwood was also asked to edit the 1885 edition, but declined, and Attfield and Bentley became associated with him, and on the completion of the work Attfield was appointed Reporter in Pharmacy to the Pharmacopœia Committee and Editor of an Addendum to the 'Pharmacopœia.' In carrying out this work Attfield succeeded in bringing about the recognised co-operation of the General Medical Council and the Pharmaceutical Society and the imperialisation of the 'Pharmacopœia,' as evidenced by the publication, under his exclusive editorship, of the 1898 edition and the Indian and Colonial Addendum, his success being largely due to the nine Annual Reports (1886–94) "On the Progress of Pharmacy in Relation to the 1885 British Pharmacopœia," prepared by him for the General Medical Council. The reports, which aptly illustrate Attfield's method and thoroughness, show how much the medical profession was indebted to pharmacists for their voluntary efforts to make the 'Pharmacopœia' a better book. Attfield received the thanks of the General Medical Council "for all that he had done to make the 'Pharmacopœia' complete and accurate."

One of the principal projects in which Attfield was interested, and of which he was one of the founders, was the British Pharmaceutical Conference, which has for its object the promotion of pharmaceutical research and of good fellowship among its members. The annual meetings of the Conference, inaugurated at Newcastle in 1863, have always been very successful, owing largely to Attfield's influence, in appreciation of which the members presented him with 500 volumes of general literature in 1880 on his retirement from official connection with the Conference as its Honorary Secretary. In addition, this Association has ever since its foundation published a 'Year-Book of Pharmacy,' containing not only a full report of its meetings, but a digest of the scientific work bearing on Pharmacy published in other countries. The editorship of this publication was entrusted to Attfield and retained by him for many years.

Attfield's views on education were always of the broadest type. He had a high opinion of the value of chemistry as a means of culture, considering that it taught the student—to quote his own words—"to observe accurately, reflect accurately, and describe accurately on all and any matters in general life."

He was a strong advocate of a curriculum of study, regarding the acquisition of knowledge merely for examination purposes as pernicious; hence he questioned any method of examining candidates which did not take note of the quality of the educational course which had been gone through. As a teacher he was pre-eminently kind and sympathetic, and the esteem in which he was held by his students may be gauged from the following extract from an address presented to Attfield in July, 1897, together with a silver tray and silver tea and coffee service, by his old pupils and friends:—

"During the whole of this long tenure of his important office Prof. Attfield not only won and retained the respect of successive generations of students by the lucidity, accuracy, and thoroughness of his teaching, but he also endeared himself to them by his unfailing tact, kindness, and urbanity. Not less successfully did he serve pharmacists and medical practitioners, and through them the public, by his versatile ability, untiring energy, and power of organisation as an editor of the 'Pharmacopœia,' and author of a manual of chemistry, and generally as a worker who unceasingly applied the resources of the great science of chemistry to the demands of the great art of healing."

A. C.

NEVIL STORY-MASKELYNE, 1823—1911.

IN view of the near approach of the 250th Anniversary of the Royal Society, it is worthy of remark that the death of Mervyn Herbert Nevil Story-Maskelyne removes from the roll of living Fellows the name of one whose father and grandfather were Fellows before him. With a short break between 1811 and 1823 these three generations held the Fellowship from 1758 to 1911, that is, for 140 out of 153 consecutive years, or for more than half the whole period during which the Society has existed.

The Maskelyne family can be traced back as landowners in Wiltshire to 1435. Though the returns for the borough of Cricklade (1625) are missing, Brown Willis states that Edmund Maskelyne (1564—1629) was M.P. for Cricklade in that year, and the same constituency was also represented by his son, Nevill Maskelyne, in 1660, and again (both before and after its conversion into the Cricklade Division of Wiltshire) by the late Mr. Story-Maskelyne from 1880 to 1892.

The introduction of the name Nevill or Nevil into the family arose from the fact that the wife of Edmund Maskelyne was grand-daughter of Mary Neville, sister of Lord Abergavenny. It was borne by many of Edmund's descendants, among whom was the celebrated Astronomer Royal. It is unnecessary to recapitulate here the claims to distinction of this well-known Copley Medallist. His only child, Margaret Maskelyne, married in 1819 Mr. Anthony Mervyn Reeve Story, who had taken a Double First at Oxford at the early age of 19, and was elected a Fellow of the Royal Society in 1823. Subsequently, Mr. Story, as owner of the Maskelyne estates in right of his wife, took the name of Story-Maskelyne, by which his descendants were thenceforth known.

His eldest son, the subject of this memoir, was born on September 3, 1823; was educated at Bruton Grammar School, in Somersetshire; entered Wadham College, Oxford, in 1842; and took his Degree with a Second Class in Mathematics in 1845. It is probable that his taste for experiment prevented his attaining higher honours, for, as an undergraduate, he had taken to the study of chemistry, which he himself sarcastically described as "an absolutely useless or rather harmful study, as distracting the mind from the degree subjects of the Schools."

He had been intended by his father for the Bar, and, after leaving Oxford spent his time between Basset Down, the family place in Wiltshire, and the Temple. The story of how science ultimately captured him is a sufficiently good illustration of the difficulties with which students of science had to contend in the forties and early fifties of the last century to be worth telling in some detail.

About two years before he went to Oxford Story-Maskelyne had become known to Dr. Buckland, who visited Basset Down to collect fossils in the great cutting in the Kimmeridge clay made between Swindon and Wootton Bassett during the construction of the Great Western Railway. By him the young man, shortly after his arrival in Oxford, was introduced to Dr. Daubeny, and thus was welcomed to the meetings of the Ashmolean Society, to which, as he believed, he was the only undergraduate then admitted. His impressions of these meetings were described by him in an autobiographical note which he wrote in November, 1908, in response to a letter from Mrs. Gordon, a daughter of Dean Buckland:—

"The discussions," he said, "were sometimes interesting, often not very interesting, to me at least, but as I felt even then, and have always felt since, these gentlemen held up the lamp of learning in natural science that had been lit more than a century and a half before by Boyle and Wren and other founders of the Royal Society. The lamp was flickering, but it has since burnt more brightly under the new conditions of its feeding."

During his undergraduate days, as has been already stated, he studied chemistry, attending Dr. Daubeny's lectures in that subject, Buckland's in mineralogy, and experimenting both in his own rooms and later in a laboratory which he established at Basset Down.

He also formed an early intimacy with Fox-Talbot, a Wiltshire neighbour, whom he frequently visited, and who was attracted by the fact that Maskelyne himself was among the first to practise the art of photography in its then stage of development. At the meeting of the British Association held in Oxford in 1847 the latter read a short paper on some of his results, and he used to relate that he showed the method of developing a photograph to Faraday, who had never seen the operation performed before. At a later period Maskelyne was recognised as an authority on the early history of photography. An anonymous article on "The Present State of Photography," which appeared in the 'National Review' in April, 1859 (No. 16, pp. 365—392, Chapman and Hall), was written by him, and he was Secretary to a Committee which reported to the British Association on the same subject in the same year ('Rep.,' 1859, pp. 103—110).

To return, however, to the "forties," Dr. Buckland was made Dean of Westminster in 1845, the year that Story-Maskelyne took his degree. While reading at the Temple the youth was a frequent visitor at the Deanery, where he met many well-known men, among whom was Sir David Brewster. How favourable the impression he produced must have been is shown by the fact that Brewster, then Principal of the University of St. Andrews, invited him to become a candidate for a Professorship there, but as the recipient of the compliment ambiguously said, "guided by parental wisdom, or in obedience to its authority, I continued my studies in a conveyancer's chambers."

But neither wisdom nor authority could for much longer restrain the young chemist from yielding to his natural bent. At the meeting of the British Association already referred to (1847) he met Benjamin Brodie, who had just returned to London after completing the Giessen course under

Liebig. This new friend, who offered the hesitating recruit an opportunity of working at chemistry in his own laboratory, induced him to give up law and to throw in his lot with science, a decision which was doubtless strengthened by his growing friendship with Faraday. Only three years later, in 1850, Dean Buckland became unable to carry on his work at Oxford, and, to his great surprise, Story-Maskelyne was asked if he would undertake the lectures on Mineralogy which had been delivered by his old friend. With becoming modesty he suggested that Brodie should have been invited in preference to himself, but when Brodie refused the invitation he consulted Faraday as to his own course of action.

"I told him," he afterwards wrote to Mrs. Gordon, "that I had collected minerals at one time and had only superficially studied them, but had no fear as regards the subject of mineralogy alone; but that crystallography was essential as the most important part of the subject, and with that I had only the slight acquaintance that the ordinary chemist was equipped with. Faraday's answer was, 'Accept the offer, and, as you have several months before you, come here (to the Royal Institution) on such evenings as you may have [free]. You shall have a room and light, and I will get from the library any books you may need.' A noble offer, need I say that I accepted it?"

His acceptance of the Oxford post was, however, subject to the condition that a laboratory should be assigned to him where he could teach Mineralogical Analysis and Chemistry in general. In answer to this request a suite of rooms was allotted to him, situate under the Ashmolean Museum and comprising six living rooms and offices, a laboratory, and a small theatre. There he lived from 1851 to 1858.

Previous to the opening of his laboratory, chemical manipulation had not been taught in the University of Oxford, and great interest was excited by the opportunity of learning what sort of thing modern chemistry might be.

The first applicant for admission was Thompson, afterwards Archbishop of York, and he was followed by Henry Stephen Smith (afterwards the well-known Savilian Professor of Geometry), Richard Congreve, Charles Pearson, and many others.

During his residence in Oxford Story-Maskelyne served as Secretary of the Ashmolean Society, and published various papers, among which may be mentioned that "On the Oxidation of Chinese Wax" ('Chem. Soc. Journ.,' vol. 5, 1853, pp. 24—26), and an "Investigation on the Vegetable Tallow from a Chinese Plant (*Stillingia sebifera*)" ('Chem. Soc. Journ.,' vol. 7, 1856, pp. 1—13; Erdmann's 'Journ. Prakt. Chemie,' vol. 65, 1855, pp. 287—296).

In addition to his scientific work Story-Maskelyne took an active part in the historic struggle for the erection of a museum in Oxford.

"There were two Delegacies," he wrote, "to which the museum question was entrusted. I was Secretary to the first Delegacy, Charles Conybeare, of Christ Church, an excellent man and an ardent supporter of the cause, was Secretary to the second Delegacy. I had collected in London a quantity of suggestions for the mode of lighting, size of rooms, etc., at the desire of the Delegacy, and the general scheme was sketched out sufficiently for a further step in discussing the actual [erection of the building]. This matter went before Convocation, and a big meeting was held in the theatre . . . [but] the proposal was thrown out. . . . Much unpleasant feeling was produced, and I think some who were in opposition became convinced they had made a mistake."

This defeat was the precursor of ultimate victory, but it is needless to tell again the tale of how, under the leadership of Sir Henry Acland, that victory was won.

In 1855 (a date wrongly given as 1865 in the new edition of the 'Encyclopædia Britannica,' p. 625) Sir Benjamin Brodie was appointed Professor of Chemistry at Oxford, and Story-Maskelyne, who was successively Deputy Reader, Reader, and Professor of Mineralogy, held also for a short time the title of Assistant Professor of Chemistry. By Brodie's appointment, however, as Maskelyne himself said, his own Chemical Laboratory became "redundant" as a University Institution. The difficulty was soon solved, for within the next two years he was appointed to the newly-established post of Keeper of the Minerals at the British Museum, in which, perhaps, the chief work of his life was done.

He continued to hold the Chair of Mineralogy at Oxford, and by inviting the most promising of his pupils to work with him in London he extended the usefulness of both offices, and trained the next generation of British mineralogists. Among the best known of these are W. J. Lewis, the Professor of Mineralogy at Cambridge; Lazarus Fletcher, who succeeded him as Keeper of the Minerals, and is now Director of the Natural History Museum at South Kensington; and Sir Henry Miers, who followed him as Professor at Oxford, and is now Principal of the University of London.

To these may be added Dr. Viktor von Lang, who, after studying for two years in the British Museum, was successively Professor of Physics at Grätz and Vienna, and was associated with Joseph Grailich in a series of Memoirs on "Crystallography," published in the 'Sitzungsberichte' of the Academy of Vienna.

On settling in London Mr. Maskelyne married a lady who was herself a member of a scientific family, being grand-daughter of Dillwyn, the well-known botanist, and daughter of Mr. John Llewelyn, of Penllergare, Swansea, who was a Fellow of the Royal Society.

For six years previous to 1857 there had been no one at the British Museum who took any special interest in Mineralogy, and it was only in that year that the special Department of Mineralogy was instituted, and Story-Maskelyne was appointed Keeper. For five years he had only one assistant, the late Mr. Thomas Davies, who came without any special training, but, fortunately, developed an extraordinary capacity for museum work, acquired an unrivalled eye-knowledge of minerals; and became a most valuable scientific assistant.

Maskelyne undertook the whole rearrangement of the collection according to the crystallo-chemical system of Rose. He busied himself much with the acquisition of specimens, and, under his direction, the collection was enormously increased and improved. He was quick to see the importance of making as complete a collection of meteorites as possible, and devoted a great deal of his time and energy to their study.

There was at that time no laboratory or equipment for scientific research. Gas was not allowed in the building, and it was therefore extremely difficult to conduct any real scientific investigation. Maskelyne's work was during these years very largely confined to what could be done with the microscope and goniometer. He was one of the first to investigate thin sections of rocks and minerals with the aid of polarised light, and was actually using a microscope, with a revolving stage and eyepiece micrometer, for the study of thin sections of meteorites, about the year 1861.

His goniometer work was carried on with great difficulty without the assistance of proper artificial light, and he always attributed the deterioration of his eyesight to the strain of this work. That he, nevertheless, managed to carry out difficult and minute crystal determinations either at the Museum or at home, is shown by the remarkable measurements made on almost microscopic crystals of Connellite, and on those of Asmanite.

By 1867 he had made it clear to the authorities that scientific research could not be carried on without a chemical laboratory, and in that year Dr. Flight was appointed as assistant, and the laboratory was fitted up in a house outside the Museum.

Maskelyne held the office of Keeper of Minerals from 1857 to 1880, and, during that period, was able not only to maintain and develop the collections, so that they became the largest and best arranged series of minerals and meteorites in existence, but also to issue, with the help of his assistants, an important series of scientific memoirs.

Among these especially noteworthy are the series of 'Mineralogical Notes' published in 1863–4, in conjunction with von Lang, and the 'Mineralogical Notices' published in 1871–4, in conjunction with Flight.

It is stated in an obituary notice in the 'Mineralogical Magazine' that, during Maskelyne's tenure of the Keepership, no less than 43,000 specimens were added to the collection. These included, among others, the well-known Koksharov Collection acquired in 1865, in connection with which Maskelyne paid a visit to Russia, in order to negotiate the purchase, and the Allan-Greg Collection (1880), which included a fine series of British minerals well catalogued.

A survey of Maskelyne's published papers shows that, up to 1855, he was chiefly interested in chemical problems, that the study of meteorites engaged his attention as soon as he went to the British Museum, and that the period of his greatest scientific activity, as a mineralogist, judged by the published papers on minerals and meteorites, ranged from 1860 to 1880.

Among the more important of the papers on meteorites may be mentioned the investigations on the Parnallee, Nellore, Breitenbach, Manegaum, Busti, Shalka, and Rowton meteorites; among mineral researches, those upon Langite, Melaconite, Tenorite, Andrewsite, Connellite, Chalkosiderite, and Ludlamite.

New minerals described by him were Andrewsite, Langite, Liskeardite, and Waringtonite, and the following constituents of meteoric stones were first isolated and determined by him: Asmanite, described in 1871 as an orthorhombic variety of silica from the Breitenbach meteorite isomorphous with Brookite, but now generally regarded as identical with the mineral Tridymite, described by vom Rath in 1868; Oldhamite, a calcium sulphide, described in 1862, from the Busti meteorite; and Osbornite, described in 1870, from the same stone. He was also the first to recognise the presence of Enstatite in meteorites.

He was always much interested in the history of the diamond, and, in a paper published in 'Nature' in 1891, returned to the history of the Koh-i-noor, on which he had first written in 1860. There was considerable stir about 1880, just before he left the Museum, concerning the artificial production of the diamond; Maskelyne proved that the supposed diamonds which had been manufactured by Mactear were in reality a crystallised silicate.

The mode of occurrence of the diamond in South Africa also occupied his attention, and he described the Enstatite rock, which is associated with it in that part of the world.

Maskelyne's views on Crystallography were first made public in a series of lectures delivered before the Chemical Society in 1874, and more fully in his well-known text-book, 'The Morphology of Crystals,' which was published in 1895 In this, as in his University lectures, the attention of students was especially called to the important subject of symmetry. From his early days this had particularly engaged Maskelyne's attention, and many of his views are no doubt the result of discussions between him and Viktor von Lang at the time when the latter was Assistant in the Mineral Department, from 1862–4. Von Lang's book, which was published in 1866, treated the subject of crystal symmetry in a novel and original manner, and Maskelyne's publications were devoted to the development of this subject on somewhat similar lines. His 'Morphology of Crystals' was published at so late a date that other methods of treatment, and another nomenclature, had become somewhat firmly established before it appeared. Had it been published when first written, it would have attracted much attention as a highly original work. Some of the proof-sheets were in the hands of his pupils for very many years before the book ultimately appeared; his views had been made known to them throughout the whole period of his professional career, and profoundly influenced their own teaching.

The chief feature of this book is the investigation of the geometrical relations of a crystalloid system of planes, that is to say, planes obeying the law of rational indices, and the most important and original part of the investigation is that which deals with the varieties of symmetry possible in such a system. The subject is developed by a study of the symmetry planes inherent in the system; the important proof concerning the number of symmetry planes possible in a crystalloid system and their mutual inclinations was, as is stated by Prof. Lewis in his 'Crystallography,' given in a course of lectures by Prof. Maskelyne as far back as 1869. The whole treatment of the subject is elegant and lucid, and the new and expressive nomenclature employed invests these chapters with a certain charm, but by the time the book appeared other investigators had begun to approach the subject of crystal symmetry from another point of view. The independent operation of axes and planes of symmetry, and the application of these operations to homogeneous molecular structures, had been adopted as a less arbitrary and more fundamental treatment. Maskelyne contemplated a second volume, which was to deal with the physical properties of crystals, and had this been written he would doubtless have elaborated and criticised the newer methods. Some portions of this book were for several years actually in print, but he never found himself sufficiently free to complete the work.

In his mathematical, as in his scientific, writings Maskelyne's work was characterised by a remarkable distinction and charm of style, which was, indeed, part of his character, and prevailed in everything that he undertook. In all his scientific work the mind and sympathies of an artist declared themselves, and were as well known to his pupils as to his personal friends.

It was therefore characteristic that his devotion to his work as Keeper of Minerals did not lead him to narrow the range of his interests to mere specialism, but to extend it to a kindred subject. A good deal of his scientific work brought him into contact with ancient art, for which he always had a great fondness, and which was fostered by his opportunities in the British Museum. In his own words "Antique gems and Greek art got hold of me as I went continually through the galleries of the British Museum on my way to my own." But though favourable circumstances undoubtedly stimulated him, his taste was shown both before and long after he was connected with the Museum. As far back as 1869, for example, he was discussing at the Society of Antiquaries the nature of the Murrhine vases of the ancients, which he believed to be composed of heated sard, in opposition to Westrop, who thought Pliny's Murrhina to be fluor. As late as 1894 he was lecturing in Wiltshire upon the subject of Greek art. In the intervening years he not only formed a very valuable private collection of antique gems, but, at the request of the Duke, produced the well-known catalogue of the engraved gems belonging to the Duke of Marlborough's collection.

A great change took place in Maskelyne's life on the death of his father in 1879. Henceforth he became an active country gentleman, though he continued to hold his office of Professor of Mineralogy at Oxford. At that date funds were not available for securing the whole time of a resident professor, and it was in the interests of the University itself that he retained office while waiting for the adequate endowment of his Chair. So soon as this was secured, by attaching the professorship to the Waynflete foundation at Magdalen College, he retired.

In 1880 he was elected in the Liberal interest as Member for Cricklade, and thereafter sat in three Parliaments, *i.e.* until 1892. Though he could hardly be called a conspicuous, he was unquestionably an active Member of Parliament. He was one of the Liberals who refused to follow Mr. Gladstone in his Home Rule policy, and without any doubt or hesitation ranged himself from the first among those who threw out the Bill of 1886. His constituency, nevertheless, returned him again to Parliament in the General Election which followed. It is not too much to say that the maintenance of the Union and of the efficiency of the Navy were two of the leading articles of his political creed. He served on several Committees, such as that concerned with the subsidences in Cheshire due to salt workings, and as a Member of the Committee on Electric Lighting he always opposed what he believed to be the harmful obstacles then thrown in the way of the development of the nascent industry. He was one of the members who supported the Commons Preservation Society, and this led to his Chairmanship of the Committee that dealt with the Thames Preservation Bill. His interest in politics did not flag after his defeat in the election of 1892, and was enhanced by the career of his son-in-law, the late Mr. Arnold-Forster.

He also took an active part in county matters, was a Member of the Wiltshire County Council from its foundation till he was over eighty years of age, and was for many years Chairman of the Agricultural Committee. He was an active Member of the Bath and West of England Agricultural Society, the presidency of which he declined, on account of his advanced years, when the meeting was held in Swindon. It was at his suggestion that the first itinerant dairy school was established.

In 1904 Mr. Maskelyne underwent a severe operation, and from that time till his death in 1911 he was always more or less of an invalid. His old age was, however, brightened by his intense mental activity and by his interest in the progress of science. In 1904, when his life was in great danger, he exclaimed: "I must live, I want to know more about radium."

He was a good scholar, and was one of the few scientific men who read Homer till late in life. The variety of his interests had brought him into contact with many of the most distinguished minds of two generations. He knew the bearers of all the best known Oxford names. He helped to entertain Liebig when he visited that University. He was the intimate friend of Charles Mansfield, the chemist, who died too young to have achieved a great popular name, but whose heroic end in a laboratory accident he could not recall without emotion. With him he worked in the social movement associated with the names of Kingsley and Maurice, and frequently lectured at the Working Men's College. At the British

Museum he was visited by many foreign mineralogists and collectors of minerals and gems. As a Member of Parliament he was on terms of friendship with Mr. Chamberlain and many other politicians. His wide knowledge of men and things, his memories of a long distant past, and his keen attention to the problems which are interesting the youth of to-day, made him a delightful companion to young and old.

To use his own words, "the twilight of his departing day" was cheered by the consciousness of having lived through a great age and by the pleasure of having "known, in different degrees, so very many of the vigorous men to whom that era is indebted for its splendour."

Mr. Story-Maskelyne was the recipient of many testimonies to his scientific worth. He was an Honorary Fellow of Wadham College, and received in 1902 the Honorary Degree of Doctor of Science from the University of Oxford. He became a Fellow of the Royal Society in 1870, served twice on the Council, and was Vice-President from 1897 to 1899. He was Corresponding or Honorary Member of the Imperial Mineralogical Society of St. Petersburg, of the Society of Natural History of Boston, of the Royal Academy of Bavaria, and of the Academy of Natural Sciences in Philadelphia.

Mrs. Maskelyne and his three daughters survive him. One of the latter married the late Right Hon. H. O. Arnold-Forster, some time Secretary of State for War, and another is the wife of Sir Arthur Rücker.

A. W. R.
H. A. M.

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